CCLXVII.—*Influence of Directing Groups on Nuclear Reactivity in Oriented Aromatic Substitutions. Part II.** *Nitration of Toluene.*

By CHRISTOPHER KELK INGOLD, ARTHUR LAPWORTH, EUGENE ROTHSTEIN, and DENIS WARD.

UNTIL four years ago, data for the proportions in which isomerides are simultaneously formed in aromatic hydrogen-substitutions contributed the only direct, quantitative experimental basis for the numerous theories of the process which had at various times been advanced. At the period mentioned the broad lines of the modern view had been laid down; and not only was this view no exception to the preceding statement, but also many theoretical details which have subsequently been filled in have arisen from the determination of further data of the same type. In 1927, however, the view that continued development of the theory would require the consideration, not only of proportions of isomerides, but also of relative velocities of substitution, led to the publication of Part I (Ingold and Shaw, J., 1927, 2918), in which data of the latter kind were submitted for a number of benzene derivatives having single orienting substituents of widely differing structural types.

Proportions of isomerides, which are also ratios of their rates of formation,† are regarded as giving only the *ratios* of magnitudes which individually relate to the effect of the substituent on reactivity at the different nuclear positions. The speed of total substitution relatively to that of benzene, in short, the " reduced " velocity of substitution, yields the *sum* of such magnitudes. Only when both the ratios and the sum are known can the individual effects be defined, and the influence of the substituent on nuclear reactivity

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* The first of these studies, called Part I in the text, was published in another series under the specific title " An Attempt further to define the Probable Mechanism of Aromatic Substitution."

† This is true provided that the simultaneous substitutions are reactions of the same order and are irreversible, which are the conditions contemplated; it is known that normally these conditions are fulfilled for nuclear nitration and halogenation.

be described. As an example, quantitative data have long been available which show that, on nitration, for instance, toluene and chlorobenzene both give very greatly preponderating amounts of *op*-isomerides; but velocity measurements show that the effects are nevertheless not parallel, *op*-reactivity being increased by the orienting substituent in the one case and diminished by it in the other; moreover, the compound with smaller *op*-reactivity gives the higher proportion of *op*-isomerides. The examples illustrate two of the very small number of recognised modes of genesis of orientation (each corresponding with a distinctive form of nuclear reactivity) which were discussed in Part I, where conclusions concerning their space- and time-relations will be found.*

In order to obtain a numerical measure of the influences of an orienting substituent on reactivity in relation to substitution at an individual nuclear carbon atom, a quantity, called the "coefficient of activation," was defined in Part I as the factor by which the introduction of the directing group increases the probability of substitution at that atom during a small element of time under the conditions of comparison. We now suggest the alternative term "partial rate factor" as a designation less likely to cause a confusion of ideas when it becomes necessary to consider the relation of these factors to critical energy increments (energies of activation). Statistical requirements must be borne in mind, but these factors are readily calculated from the proportions of simultaneously-formed isomeric substitution products and the reduced velocity of the total substitution.

In Part I, no attempt was made to establish standard values for the reduced velocities or partial rate factors, because these were found to vary so greatly from case to case as to render that unneces-

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* These have since been developed, in that the idea, which was only lightly touched upon in Part I (p. 2918, footnote), of regarding the external field as contributing, along with the internal field, to the permanent state of polarisation, was made definite a few months later (Ingold and Vass, J., 1928, 417; compare Lapworth and Robinson, *Mem. Manchester Phil. Soc.*, 1928, **72**, No. 4), and has been explicitly embodied in subsequent restatements (*e.g.*, *Rec. trav. chim.*, 1929, **48**, 797). Pursuing the examples in the text, the nuclear activation of toluene and deactivation of chlorobenzene are now attributed to the collaboration of the internal and external contributions to the permanent polarisation $\pm (I + D)$.

One further amendment, also in the nature of according explicit recognition to a factor which in 1927 was only suspected, is now necessary. This concerns the time-variability of the electromeric (tautomeric) effect (T), and arises from the circumstance that the possibility (indicated in parentheses in Part I, p. 2923, line 25) of a static residuum has since become a very definite probability (dipole moments, recent data).

The authors of Part I wish it to be understood that their present views embody these developments.

sary in a preliminary general survey of the field. The case of toluene, however, is of rather special interest from a theoretical view-point, and it has since been studied in some detail.

The definition of partial rate factor clearly implies the possibility of the variation of this magnitude with experimental conditions of the substitution, and one of the general questions we hoped to answer by a detailed study of the nitration of toluene concerns the extent of this possible dependence on conditions. The experimental conditions which are most likely to be of importance in this connexion are: (1) the nature of the nitrating agent, (2) the composition, and relative quantity, of the solvent, and (3) the temperature; and although the whole of the intended ground has not yet been covered, we are able to submit the following evidence.

First, we have determined the reduced velocity, and the partial rate factor, to the limits of accuracy of the available analytical methods for one particular group of experimental conditions, namely, for nitration by acetyl nitrate, either in acetic acid alone as solvent, or in the presence of various excesses of acetic anhydride, at 30°. We find that there is little if any change in these constants to correspond with the changes in the composition and proportion of solvent within the range indicated (condition 2, above). Secondly, treating the above group of conditions as a point of departure for more extended alterations, we have (*a*) changed the nature of the nitrating agent and solvent altogether (conditions 1 and 2), retaining the above temperature, and (*b*) changed the temperature (condition 3), retaining the original nitrating agent and solvent; but, at present, we are able to submit only approximate determinations corresponding to these changes. It will be understood that the necessity for maintaining homogeneous solutions in measurements of velocity considerably limits the choice of solvents, whilst the stabilities of reagent–solvent mixtures and the reaction velocities themselves both limit the available temperature range. As to (*a*), the reagent and solvent were altered to nitric acid in nitromethane, and as to (*b*), the temperature was changed to 0°. Alteration (*a*) led to the reduced velocity, and to coefficients of activation which were identical with those pertaining to the standard conditions to well within the presumed limits of precision. Alteration (*b*) yielded a slightly higher reduced velocity and generally higher coefficients of activation; but the differences were small, and are revealed most clearly by a statistical consideration of the results. In this connexion, mention may be made of a speculation, which, to some extent, is encouraged by the discovery (Bradfield and Jones, J., 1928, 1006, 3073; Bradfield, Jones, and Orton, J., 1929, 2810) that in *o*- or *p*-substituted alkyloxybenzenes the two substituents contribute characteristically and additively to the logarithm of the velocity of nuclear halogenation; it is that the partial rate factor (F) may vary with temperature in such a way that $\Delta E = RT \log_e F$ is constant or approximately constant. The hypothesis implies that the ΔE's might be interpreted as differences between the activation energies of the partial reactions (*e.g.*, of toluene and benzene) to which the F's relate, or, in other words, that they measure the "internal activation" by the substituent (*e.g.*, methyl) for the partial nuclear reactions of the benzene derivative (*e.g.*, toluene). Our results are not inconsistent with this suggestion, but more accurate data will be required finally to prove or disprove it. For the present, the conclusion is merely that the investigated alterations in the nitrating agent, in the solvent, and in the temperature, lead to no great change either in the values of F or in those of ΔE.

For the most fully investigated group of conditions (nitration by acetyl nitrate at 30°) the reduced velocity was found to be 23. The derived values of F and of ΔE (the latter in kg.-cal.) are as follows:

$$F_{\text{ortho}} = 40 \qquad F_{\text{meta}} = 3{\cdot}0 \qquad F_{\text{para}} = 51$$

$$\Delta E_{\text{ortho}} = +\ 2{\cdot}21 \qquad \Delta E_{\text{meta}} = +\ 0{\cdot}66 \qquad \Delta E_{\text{para}} = +\ 2{\cdot}36$$

For the other sets of conditions all values are identical with the above, except the last significant figure, which in these cases may not be accurate (see Table XVIII).

From the figures in the table, it is seen that the speed of substitution in all the nuclear positions of toluene, including the *m*-positions, is increased (the corresponding speculative statement is that all positions, including meta, are internally activated by the methyl group); and to this extent the results support the conclusion in Part I relating to the origin of the meta-substitution product to which the nitration of toluene gives rise.

(By ARTHUR LAPWORTH.)

The writer, with one of his pupils, had been carrying out experiments on nitration of toluene for nearly a year on lines somewhat similar to those adopted by Ingold and Shaw when their communication (Part I, *loc. cit.*) appeared. A generous offer was made to him that further work on the subject should be done in collaboration, but he has to confess that his contribution towards the laborious and careful work described in the experimental section has been but slight. He approaches the theoretical aspects of such work from a standpoint appreciably different from that of his colleagues, and in the circumstances some statement of his attitude to certain points raised in this paper and in Part I seems necessary.

Dimethylaniline is but incompletely sulphonated when heated with 5 molecular proportions of ordinary sulphuric acid for 12 hours at 180° (Evans, P., 1895, **11**, 235). Yet, as is well known, benzene is readily sulphonated by this agent even at 100°. In order to bring about substitution in dimethylaniline in presence of excess of sulphuric acid at 100°, the potency of the sulphonating agent must be raised by addition of sulphuric anhydride, in which case a large proportion of meta-sulphonic acid is formed.

This clearly shows that conversion of the dimethylamino-group into the salt-constitution, where it functions mainly as a meta-directive group, is associated with a complete or almost complete deactivation of the meta-positions as well as the ortho- and para-positions towards ordinary sulphuric acid, which is quite incompatible with any doctrine demanding that introduction of a substituent into the nucleus of benzene gives rise to an alternate increase and decrease in the speed of substitution at the positions taken in order round the nucleus.

Armstrong, in discussing these and other data (P., 1899, **15**, 178), did not specifically direct attention to this self-evident conclusion. If, however, his brief statement be read in conjunction with Miss Evans's statement, to which he makes precise reference, it will hardly be doubted that his idea was substantially the same as that which is probably held by most authorities on aromatic substitution at the present time, namely, that meta-directive substituents may exercise a depressant effect on substitution at all positions in the aromatic nucleus, but less at the meta-positions than elsewhere.

Whilst it is true that those monosubstitution derivatives of benzene which are most highly resistant to substitution yield large proportions of meta-diderivatives, and that those which most readily suffer substitution yield mainly ortho- and para-derivatives, evidence is lacking that any exact parallelism exists between velocity of substitution and "directive power." There is, in fact, proof to the contrary, as some halogeno-derivatives of benzene are attacked more slowly than benzene but nevertheless yield only very small proportions of meta-nitro-derivatives. Explanations have been offered of their apparent departure from a general rule (compare Ingold and Shaw, *loc. cit.*, pp. 2918, 2922, 2923; Shoppee, J., 1930, 969), and the present author favours the idea that both in toluene and in chlorobenzene the inherent tendency of all the nuclear carbon atoms to react with a substituting agent which comes within their sphere of influence is greater than in benzene, but that the field external to the molecule of chlorobenzene opposes the outward movement of the electrons in the first stage of the actual process of substitution. These ideas are speculative; but the circumstance that no other kind of explanation can be offered at the present juncture makes it desirable to maintain reserve in deducing from "partial rate factors" of orders so small as 2, 3, or even 100, any conclusions relating to the electron density, or fugacity at the atoms in the aromatic nucleus.

The writer follows Conant and his co-workers (*J. Amer. Chem. Soc.*, 1925, **47**, 480) in believing that comparison of reaction velocities of two different molecules with a given agent is at present of little service from the theoretical standpoint unless the ratio of velocities is very large.

Nevertheless, any comprehensive theory of the relationship between reaction velocity, temperature coefficients, and "directive effects" must ultimately be qualitatively and quantitatively consistent with data such as are submitted in the present paper, and, for this reason, these data will have a value which is not in the least affected by any divergence of opinion as to their present theoretical tractability.

EXPERIMENTAL.

(1) *General.*

(1, i) *Preliminary Considerations.*—The measurements here recorded are designed to yield two kinds of data applying to correlated experimental conditions. The first relates to the ratio of the rates of substitution of toluene and benzene in simultaneous nitration. This is, in general, not the same as the ratio of the quantities of the mononitration products of toluene and benzene formed simultaneously in a finite time-period, but it may be calculated therefrom if certain auxiliary data are known. The principal experimental measurement is, however, the quantity-ratio, and this was made by two completely independent methods. The first (Section 2) involved measurements of a physical property, *viz.*, density, of the mixed mononitration product; and the second (Section 3) consisted in observations of the amount of bromine taken up by the mixed amines formed from this product by reduction.

The second group of data relates to the ratios of the speeds of formation of the isomeric mononitrotoluenes, and these are the same as the ratios of the quantities of isomerides simultaneously formed. These measurements were also made by two completely independent methods. The first (Section 4) involved oxidation of the mixtures of nitrotoluenes to nitrobenzoic acids, and analysis of these by determination of their solubility in solutions saturated with respect to two isomerides; and the second (Section 5) consisted in the application of thermal analysis, after a preliminary study of the ternary freezing-point diagram for the three isomeric nitrotoluenes.

With regard to the experimental conditions of nitration, we have studied the effect of alterations of the nitrating agent, the medium, and the temperature. Practical considerations render these factors to some extent interdependent. For instance, the solvent employed in conjunction with a given nitrating agent must be such as to ensure a homogeneous solution at all stages of nitration, since otherwise ratios of quantities can yield no information as to ratios of rates. One nitrating agent used was acetyl nitrate, which was employed in conjunction with acetic acid only as solvent, and also with various amounts of acetic anhydride. Absolute nitric acid was taken as a second nitrating agent, but some difficulty was experienced in the choice of a solvent for it, since many are attacked or fail to maintain homogeneity, and some, like acetic acid, promote side reactions in which the nitric acid oxidises, and/or nitrates, toluene in the side chain. Two solvents, *viz.*, acetonitrile and nitromethane, were, however, found which led to smooth, homogeneous nuclear nitration, without side reactions; but in the first of these the velocities were rather inconveniently low, and therefore only nitromethane was used in the quantitative experiments. Reaction velocities, and the stability of nitration solutions, restrict the available temperature range, and we found 30° and 0° near the limits of convenience for our reagents and solvents.

(1, ii) *Materials.*—Benzene and toluene, both free from sulphur, were purchased. The former was stated to be pure and suitable for direct use in *M.W.* determinations, and it had a sharp f. p. It was, therefore, used without further treatment. All our samples of toluene, however, although purchased as pure, had distinct b. p. ranges (usually exceeding 1·0°), and they were therefore purified by partial freezing; the recovered material, about one-quarter of the original, was dried with calcium chloride and with sodium, and redistilled. This greatly improved the b. p., and we have experimental evidence that without this purification our results would have been much less consistent than they are. The precaution was deemed necessary for a reason which may be illustrated by the statement that, if in the experiments recorded in Section 3 the toluene had contained 0·1% of a much more rapidly substituting impurity (*e.g.*, a homologue), the nitrotoluenes produced might have contained up to 2·5% of unrecognised impurities.

The purchased nitric acid was free from sulphur and halogens, and had *d* 1·52. In some experiments it was used directly, whilst for others it was redistilled with excess of pure sulphuric acid before use. The acetic anhydride, which was purchased, was free from phosphorus, whilst the nitromethane, prepared by ourselves, was carefully purified and dried. Possible effects due to nitrous acid are dealt with specially in Section 3 (vi).

(1, iii) *Nitrations.*—(*a*) *By acetyl nitrate.* The acetyl nitrate solution was prepared below 0° using either anhydrous nitric acid or acid of *d* 1·520. If no excess of acetic anhydride was to be present, the amount of this taken was the equivalent of the anhydrous nitric acid or of the nitric acid and water present in the aqueous acid of *d* 1·520; and predetermined excesses of acetic anhydride were calculated, in either case, on the same basis. The nitration reagent mixture was kept at 0° until just before it was required, and then (after a partial temperature adjustment for nitrations at the higher temperature) was added as rapidly as possible either to a mixture of benzene and toluene (in the experiments of Sections 2 and 3), or to toluene alone (in those of Sections 2, 4, and 5). During the addition, and for 2 hours thereafter, the mixture was rapidly stirred and the temperature was adjusted by surrounding the flask with water, ice, or a freezing mixture, as required. The product was worked up as described in Sections 2—5. The temperatures usually varied by a few degrees, but we endeavoured to maintain a constant upper limit of temperature, and it is that which is quoted in the relevant tables.

(*b*) *By nitric acid.* A mixture of anhydrous nitric acid and dry nitromethane was used for nitration in the same manner as the acetyl nitrate solution (Section 1, iii, *a*), except that 20 hours were allowed for the progress of nitration. The product was worked up as described in later sections. During the course of these nitrations a deep red colour was developed which could be destroyed at any time by the addition of water. This appears to be a general phenomenon in the nitration of aromatic hydrocarbons by nitric acid and nitromethane, which, without the hydrocarbons, give no colours or marked thermal effect on admixture. A similar, but less pronounced colour accompanies nitration by nitric acid in acetonitrile, and this also disappears as soon as the reaction is arrested by the addition of water. It is hoped later to investigate these colours in relation to the part played by such solvents in nitration.

(2) *Relative Rates of Nitration of Toluene and Benzene* (*Density Method*).

(2, i) *Preparation of Samples.*—(2, i, *a*). The nitration product (Section 1, iii, *a*) was poured on ice, and the mixture, after being kept over-night to ensure decomposition of the acetic anhydride, was extracted three times with pure ether. The extract was washed with water and with sodium hydrogen carbonate until free from acid, and then twice more with water. All aqueous washings were extracted with a little ether, and the extract was washed with a little sodium hydrogen carbonate and water, and combined with the main extract. After being dried, the bulk of the ether was removed by slow distillation through a tall column, and the residue was distilled to constant density (Section 2, ii).

(2, i, *b*). The nitration product (Section 1, iii, *b*) was poured into water, and extracted well with pure ether. The extract was treated as described in the preceding paragraph, except that the washing with sodium hydrogen carbonate was replaced by three washings with 10% sodium hydroxide in order to remove the nitromethane.

(2, ii) *Distillation to Constant Density.*—This method was used by Ingold and Shaw (*loc. cit.*), but we have improved the process with the aid of a special still-head, which permits a more accurate isolation of the mononitration product. The mixture, consisting of a little ether, much benzene and toluene, smaller amounts of nitrobenzene and nitrotoluenes, and a little " residue " (coloured matter possibly containing dinitro-products), was distilled under reduced pressure. The still consisted essentially of a Claisen flask, the bent limb of which was replaced by a sealed-on water-jacketed fractionating column. The lower half of this was an ordinary jacketed column, but the upper portion was a double-surface column and both the inner and the outer surface were furnished with jackets. Through these jackets constant-temperature water could be passed, and, for each distillation pressure, suitable jacket temperatures were known. The distillations occupied about 2 hours, during which the flask was immersed up to the bottom of the single-surface column in glycerol at 70—90°; the pressures were usually between 13 and 18 mm. By weighings and density measurements it was shown that this process completely eliminates ether, benzene, and toluene, without any appreciable loss of nitro-compounds. These nitro-compounds (containing " residue ") were now distilled, at 5—9 mm., from a small Claisen flask through a long water condenser, which was furnished with a means of rapidly altering the temperature of the water, and was cleared at the end of the process with warm water from the crystallised *p*-nitrotoluene. In order to avoid loss of the latter, the flask, whilst still in the glycerol bath, was at this stage swept out with dry carbon dioxide at about 0·5 atm., and for the same reason the side arm and condenser were finally washed out with the whole distillate. The density was found, and the process repeated until it remained unaltered by further repetition. In the case of the nitrations at 0° the " residue " was seen, after the first distillation at 5—9 mm., as a dry dark stain; in nitrations at 30°, it appeared as a small patch of tar, but a second distillation reduced it to a dry stain.

(2, iii) *Density Determinations.*—Glass pyknometers (10 c.c.) were used with similar counterpoises. The settings were made in a thermostat, which throughout the whole series of measurements worked within the range 30·25° ± 0·05°. The standard of reference was boiled-out distilled water at the same temperature. Since all that was required from these measurements was an empirical analytical index, we did not correct for buoyancy and have not reduced the observations to the standard form d_{4°.

(2, iv) *Density-composition Relation.*—Benzene and toluene were nitrated under the conditions indicated in cols. 3, 4, and 5 of Table I, and the products were distilled to constant density (col. 6). The products of nitrations 4, 5, and 6, and that of nitration 1, were used to make mixtures, the densities and compositions of which are given in Table II.

TABLE I.

Expt. No.	Hydrocarbon.	Reagent.	Solvent.	Temp.	*d.**
1	Benzene	$AcNO_3$	Ac_2O	0°	1·1986
2	,,	HNO_3	$MeNO_2$	30	1·1989
3	Toluene	$AcNO_3$	Ac_2O	0	1·1524
4	,,	,,	,,	0	1·1524
5	,,	,,	,,	0	1·1520
6	,,	,,	,,	0	1·1523
7	,,	,,	,,	30	1·1523
8	,,	,,	,,	30	1·1524
9	,,	HNO_3	$MeNO_2$	30	1·1529
10	,,	,,	,,	30	1·1528

* Uncorrected (see above).

TABLE II.

$C_6H_5\cdot NO_2$, weight %	0·00	1·40	3·84	6·39	9·60
Density	1·1523	1·1528	1·1539	1·1550	1·1565
$C_6H_5\cdot NO_2$, weight %	10·69	17·23	23·21	59·60	100·00
Density	1·1570	1·1599	1·1626	1·1701	1·1986

The data contained in Table II give an accurately linear plot ($d = 1{\cdot}1523 + 0{\cdot}000463\ p$), of which the portion utilised in this work is that between 0% and 15% of nitrobenzene. Strictly, the curve applies only to nitrations with acetyl nitrate at 0°, but reference to Table I, nitrations 7 and 8, shows it can also be used to analyse products of nitration by the same reagent at 30°. Similarly, the curve can be used for the products of nitrations with nitric acid in nitromethane at 30°, provided that the correction, 1·2%, deduced from nitrations 9 and 10, be subtracted.

(2, v) *Constancy of Composition.*—It was necessary to show, not only that the process of distillation to constant density eliminated all substances other than the mononitro-hydrocarbons, but also that it did not create some systematic alteration in the internal composition of the latter. The following tests may be quoted as evidence of this.

The artificial mixture (18 g.) having *d* 1·1550 (Table II) was mixed with 18 g. of benzene and 1 g. of toluene, and the whole was then put through the standard distillation process. The densities were : 1st dist., 1·1548; 2nd dist., 1·1550; 3rd dist., 1·1550.

The artificial mixture (10 g.) having *d* 1·1599 (Table II) was mixed with 1 g. of benzene and 10 g. of toluene, and the whole was similarly distilled. The densities were : 1st dist., 1·1597; 2nd dist., 1·1597.

(2, vi) *Results : Yields and Compositions of Mononitro-products (Density Method).*—These are recorded in Table III, cols. 2, 3, and 4 of which relate to the conditions of nitration (reagent, solvent, temperature). Col. 5, in conjunction with the footnote, indicates the quantities of benzene and toluene which were nitrated together. Col. 6 records the yields of total mononitro-products, col. 7 their densities after distillation to constant density, and cols. 8 and 9 the compositions calculated therefrom in accordance with the data of Section 2, iv.

TABLE III.

					Mononitro-products.			
							Nitrobenzene.	
Expt. No.	Re-agent.	Excess Ac_2O (g.-mols.).	Temp.	Initial benzene* (g.-mols.).	Total (g.-mols.).	*d.*	Wt. %.	Mols. %.
11	$AcNO_3$	1·00	0°	1·00	0·48	1·1542	4·3	4·8
12	,,	1·00	0	1·00	0·52	1·1543	4·4	4·9
13	,,	1·00	0	1·00	0·50	1·1541	4·2	4·6
14	,,	1·00	0	1·00	0·50	1·1544	4·6	5·1
15	,,	0·10	30	1·00	0·16	1·1544	4·6	5·1
16	,,	1·00	30	1·00	0·63	1·1550	5·1	6·7
17	,,	1·00	30	1·00	0·66	1·1550	5·1	6·7
18	,,	1·00	30	1·00	0·64	1·1554	6·9	7·6
19	,,	1·00	30	1·00	0·67	1·1556	7·3	8·0
20	,,	1·00	30	1·00	0·66	1·1551	6·6	7·2
21	,,	1·00	30	4·00	0·20	1·1587	14·3	15·6
22	,,	1·00	30	4·00	0·20	1·1587	14·3	15·6
23	,,	1·00	30	4·00	0·18	1·1588	14·5	15·8
		$MeNO_2$ (g.-mols.).						
24	HNO_3	0·75	30	1·00	0·25	1·1549	4·6	5·1
25	,,	0·75	30	1·00	0·25	1·1550	4·8	5·3
26	,,	1·50	30	1·00	0·15	1·1548	4·4	4·8

* Initial toluene = 1·00 g.-mols. throughout.

(2, vii) *Calculations : Relative Speeds of Nitration (Density Method).*—If x mols. of benzene and y mols. of toluene are nitrated together, in time t, to form Y mols. of total nitration product, containing $100P$ mols.% of nitrobenzene, then the equation

$$k_y/k_x = (\log y/y_t)/(\log x/x_t)$$

where $x_t = x - PY$, and $y_t = y - Y + PY$, holds independently of whether or not the reaction is complete at time t (Ingold and Shaw, *loc. cit.*, gave the special case of this for $t = \infty$). The substances to which the velocity coefficients, k, refer are denoted by the subscripts.

In order to facilitate appreciation of the errors involved, we have, in the first instance, calculated the velocity ratio in the percentage form $100k_x/(k_x + k_y)$, because the error in this is approximately the same as in the experimentally determined percentage quantity $100P$, where, as in the majority of these experiments, equal molar quantities of benzene and toluene are taken initially. When an excess of benzene is taken, the calculated velocity percentage becomes correspondingly more accurate.

Cols. 3, 4, and 5 of Table IV contain the observational quantities x, P, and Y ($y = 1$ throughout) for the nitrations studied by the density method; and col. 6 gives the calculated values of $100k_x/(k_x + k_y)$. An examination of these yields no evidence that the velocity ratio is appreciably affected by the different degrees of dilution of the nitration solutions, and therefore the experimental conditions are grouped in col. 2 into three sets according to the nitrating agent and the temperature. For each of these three sets of conditions we give, in cols. 7 and 8, the weighted averages of $100k_x/(k_x + k_y)$ and the probable errors in this function. Of the two major alterations of conditions shown in col. 2, namely, the alteration in the nitrating agents and the alteration in temperature, only the change of temperature affects the velocity ratio by an amount which appears to be in excess of the presumable error.

TABLE IV.

No.	Conditions.	x.	10^2Y.	10^2P.	$10^2k_x/(k_x+k_y)$.	Mean.	Error.
11	$AcNO_3$ in Ac_2O at 0°	1	48	4·8	3·7	3·7	±0·1
12		1	52	4·9	3·7		
13		1	50	4·6	3·5		
14		1	50	5·1	3·9		
15	$AcNO_3$ in Ac_2O at 30°	1	16	5·1	4·7	4·45	±0·1
16		1	63	6·7	4·6		
17		1	66	6·7	4·6		
18		1	64	7·6	5·1		
19		1	67	8·0	5·4		
20		1	66	7·2	4·9		
21		4	20	15·6	4·0		
22		4	20	15·6	4·0		
23		4	18	15·8	4·1		
24	HNO_3 in $MeNO_2$ at 30°	1	25	5·1	4·5	4·5	±0·1
25		1	25	5·3	4·7		
26		1	15	4·8	4·4		

The two experiments recorded in Part I for nitration with acetyl nitrate at 30° gave 5·7 and 6·2 for the percentage k-ratio.

(3) *Relative Rates of Nitration of Toluene and Benzene (Reduction Method).*

(3, i) *Reduction of Nitro-compounds.*—Titanous chloride was used. The incomplete recoveries which were initially experienced were traced partly to slow and incomplete reduction in the presence of excess of benzene and toluene, and partly to the absorption of material in the rubber employed; and this necessitated rapid mechanical stirring throughout reduction, and the elimination of rubber from the principal joints.

Two 5-litre Pyrex flasks were transformed as follows. A glass spiral-ribbon stirrer, of moderately large surface and steep pitch, was inserted into the flask, the neck of which was then drawn out to form the mercury seal, and lower bearing, of the stirrer. The neck below the mercury seal was provided with a water jacket. Into the flask, near the original neck, a second neck was sealed, the upper end of which supported a double-surface condenser by a well-fitting ground-glass joint. The upper end of the condenser supported a small gas-washing bulb.

The nitration products (Section 1, iii, *a*) were reduced without isolation of the nitro-compounds. Artificial mixtures of nitrobenzene and nitrotoluenes were also reduced, and in these cases benzene and toluene were added to the reduction mixtures in order to simulate the conditions of the reduction of nitration products. For artificial mixtures containing g grams of nitro-compounds, $(50g + 200)$ c.c. of titanous chloride (150 g./l.), and the same volume of concentrated hydrochloric acid, were used; and for the reduction of nitration solutions the quantities of reagents were calculated on the same basis, allowance being made for the maximum amount of nitration theoretically possible. Water was circulated in the condenser jackets, and the flasks were heated on water-baths for 48 hours with continuous stirring. The gas-washing bulbs contained a little alcohol, which was returned to the flasks after 24 hours, and again after 36 hours.

(3, ii) *Preparation of Samples.*—The contents of the reduction flasks were transferred to 5-litre Pyrex distillation flasks, washed in with 1 l. of water, and distilled in steam in such a way as considerably to reduce the volume. The fitting which closed the flask was provided with a mercury-sealed stirrer and a delivery funnel, by means of which excess of concentrated sodium hydroxide was now added to the well-stirred liquid, the lower end of the inclined condenser having previously been fitted with an adapter dipping under 200—300 c.c. of concentrated hydrochloric acid. The passage of steam was then resumed and continued for 1 hour after the complete disappearance of milkiness in the condenser. The distillate was now distilled from a water-bath nearly to dryness in a stream of carbon dioxide under reduced pressure, basified, with stirring and efficient cooling, under ether, and extracted 6 times with ether. After being dried, the ether was removed by slow distillation through a tall column, and the residue was completely distilled under reduced pressure.

(3, iii) *Bromine Equivalent of Bases.*—Francis and Hill's method (*J. Amer. Chem. Soc.*, 1924, **46**, 2498) was used, but it was found necessary to adopt very definite conditions in order to obtain correct results in the present application.

A mixture of a solution (15 c.c.) of potassium bromate and bromide (about 3·5 and 15 g./l. respectively), pure alcohol (10 c.c.), ice, 65% sulphuric acid (5 c.c.), and concentrated potassium iodide solution (4 c.c.) was titrated with 0·1*N*-sodium thiosulphate solution. When the colour of the iodide had nearly disappeared starch was added and the titration continued until the purple colour changed to brown. A standard solution (10 c.c.) of freshly distilled aniline (5—10 g./l.) in pure alcohol was treated with ice and a quantity of the bromide–bromate solution calculated, on the basis of a preliminary titration, to leave an excess of this reagent equivalent to 2—3 c.c. of the thiosulphate solution. The mixture was acidified with 10 c.c. of 50% sulphuric acid, kept, with shaking, in ice and water for 25 mins., treated with a further 2 c.c. of bromate solution, and, after addition of potassium iodide, titrated with thiosulphate as rapidly as possible (adding starch as usual) to the point at which purple disappeared from the tint of the solution. The experimental sample of bases was titrated in the same way, except that about 1·3 g. were taken, and that the amount of bromate taken was adjusted (also on the basis of a preliminary titration) to make the final thiosulphate titre 5—6 c.c. It may be noted (*a*) that, if the titration with thiosulphate is continued beyond the tint which throughout these experiments we accepted as an indication of the end-point, a brown colour persists for some 0·3—0·5 c.c., (*b*) that if the adjusted solution is kept for a short time the purple colour returns, (*c*) that the end-point is more easily discerned in the titration of mixed bases of high aniline content (*e.g.*, 15%) than if the aniline content is low (*e.g.*, 5%).

A mixture, consisting of 100α % by weight of aniline, together with toluidines containing 100μ % of the meta-isomeride, should reduce $\{2{\cdot}987 + 2{\cdot}169\alpha + 1{\cdot}493\ (1 - \alpha)\mu\}$ times its own weight of elemental bromine. Hence α can be evaluated if μ is known; and the determination of μ is described in Sections 4 and 5. (A knowledge of μ was in any case necessary for the calculation of coefficients of activation.)

(3, iv) *Error of Analysis.*—The above procedure (Section 3, iii) depends to some extent on visual judgment, and it was therefore felt necessary to ensure that the standard technique, once established, should not suffer undetected change during the period occupied by the measurements. To this end the latter were interspersed throughout this period by analyses of artificial mixtures, and the results of these tests, in chronological order, are given in Table V, all percentages being by weight. In order that each test should embrace the whole analytical procedure, nitro-compounds (not amines) were mixed, and benzene and toluene were also added before reduction. The mixtures were made in two ways; either carefully purified purchased specimens of nitrobenzene and the three nitrotoluenes were mixed, the nitrotoluenes being taken in approximately the proportions in which they would be formed in nitration, or nitrobenzene and mixtures of the nitrotoluenes, each prepared by nitration of our own benzene or toluene (Section 2, iv), were employed. Purchased materials were used for Expts. 31—34, 40, 42—44, 47 and 48; Expts. 35—39 were carried out with the products of Expts. 1 and 3—6 (Section 2, ii); and Expts. 41, 45, and 46 with the products of Expts. 1, 7, and 8 (Section 2, ii).

TABLE V.

Expt. No.	31	32	33	34	35	36
Nitrobenzene (Fd.)	48·3	6·9	6·7	4·5	6·4	9·4
„ (Calc.)	49·2	7·2	7·0	5·9	5·7	8·5
Difference	−0·9	−0·3	−0·3	−1·4	+0·7	+0·9
Expt. No.	37	38	39	40	41	42
Nitrobenzene (Fd.)	9·7	9·2	9·0	5·4	3·3	3·9
„ (Calc.)	9·8	9·2	7·9	6·2	3·8	4·3
Difference	−0·1	±0·0	+1·1	−0·8	−0·5	−0·4
Expt. No.	43	44	45	46	47	48
Nitrobenzene (Fd.)	6·6	4·2	18·0	13·3	12·4	9·4
„ (Calc.)	7·5	3·7	18·6	12·6	13·5	9·4
Difference	−0·9	+0·5	−0·6	+0·7	−1·1	±0·0

A large number of the samples of mixed bases obtained in the experiments of this and the following sections were tested for chlorine (sodium-fusion and Carius methods), but all were completely free from this element.

(3, v) *Results: Yields and Compositions of Amines* (*Reduction Method*).—These are in Table VI, the headings of which require no explanation. The nitrating agent was acetyl nitrate and the initial quantity of toluene was 1 g.-mol. throughout.

(3, vi) *Effect of Oxides of Nitrogen.*—Special experiments were made to determine whether the presence in the nitration solution of nitrogen trioxide or of the oxides into which it dissociates was an essential factor determining the results. The data given by these experiments are included in Table VI.

Three parallel nitrations were carried out, one (No. 66) in the ordinary way, one (No. 65) in the presence of urea, and one (No. 67) in the presence of a copious stream of oxides of nitrogen, stoicheiometrically equivalent to nitrogen trioxide, generated from arsenious

TABLE VI.

Expt. No.	Temp.	Excess Ac_2O (g.-mols.).	Initial benzene (g.-mols.).	Monoamino-products.		
				Total (g.-mols.).	Aniline.	
					Weight %.	Mols. %.
51	0°	0·00	1·00	0·24	3·9	4·5
52	0	0·00	1·00	0·24	2·9	3·4
53	0	1·00	1·00	0·66	4·8	5·4
54	30	0·00	1·00	0·28	3·2	3·7
55	30	0·00	1·00	0·24	3·9	4·5
56	30	0·00	1·00	0·26	4·3	4·9
57	30	0·00	1·00	0·30	3·5	4·0
58	30	0·00	1·00	0·34	4·6	5·2
59	30	0·00	1·00	0·36	3·8	4·4
60	30	1·00	1·00	0·66	6·1	6·9
61	30	1·00	1·00	0·64	5·9	6·7
62	30	1·00	1·00	0·66	6·1	6·9
63	30	2·00	1·00	0·24	4·9	5·7
64	30	2·00	1·00	0·56	4·5	5·2
65	30	3·00	4·00	0·17	11·3	12·8
66	30	3·00	4·00	0·10	9·8	11·3
67	30	3·00	4·00	0·06	11·7	13·2
68	30	5·00	4·00	0·09	14·3	16·2
69	30	5·00	4·00	0·04	10·0	16·4
70	30	6·00	5·00	0·10	16·3	18·3
71	30	6·00	5·00	0·07	16·6	18·7
72	30	6·00	5·00	0·07	16·7	18·8

oxide and aqueous nitric acid. The results are not noticeably more diverse than are those of other parallel sets shown in the table.

A pair of parallel nitrations (Nos. 68 and 69) were carried out, to one of which (No. 69) urea was added. The results are almost identical.

These experiments, therefore, reveal no effect due to oxides of nitrogen.

(3, vii) *Calculations: Relative Speeds of Nitration* (*Reduction Method*).—The formulæ of Section (2, vii) are used, in which Y is now interpreted as the molar yield of total amines, and P as the mol.-fraction of aniline contained therein. The values of the percentage velocity ratio, $100k_x/(k_x + k_y)$, are shown in col. 6 of Table VII, the headings of which correspond with those of Table IV ($y = 1$ throughout). Examination of the long set of velocity values relating to the temperature 30° (the set relating to 0° is too short to be of service in this connexion) reveals no definite effect due to different degrees of dilution of the nitration solution or to the presence or absence of free acetic anhydride, and, accordingly, the experimental conditions are broadly grouped as is shown in col. 2. In explanation of the figures in col. 4, it should be stated that, if Y is small, the velocity ratio is not sensitive to its absolute magnitude, and one significant figure, where only one is quoted, is quite sufficient for the calculation of the k-ratio to two significant figures. Cols. 7

and 8 contain the weighted average values of $100k_x/(k_x + k_y)$ and the probable errors in these quantities.

TABLE VII.

No.	Conditions.	x.	10^2Y.	10^2P.	$10^2k_x/(k_x+k_y)$.	Mean.	Error.
51	$AcNO_3$ in Ac_2O at 0°	1	24	4·5	4·0	3·5	±0·3
52		1	24	3·4	3·0		
53		1	66	5·4	3·6		
54	$AcNO_3$ in Ac_2O at 30°	1	28	3·7	3·2	3·95	±0·1
55		1	34	4·5	3·8		
56		1	26	4·9	4·3		
57		1	30	4·0	3·5		
58		1	34	5·2	4·5		
59		1	36	4·4	3·8		
60		1	66	6·9	4·8		
61		1	64	6·7	4·7		
62		1	66	6·9	4·8		
63		1	24	5·7	5·1		
64		1	56	5·2	4·1		
65		4	17	12·8	3·3		
66		4	11	11·2	2·9		
67		4	6	13·2	3·6		
68		4	9	16·2	4·4		
69		4	4	16·4	3·1		
70		5	10	18·3	4·1		
71		5	7	18·7	4·2		
72		5	7	18·8	4·2		

(4) *Proportions of Isomerides Formed in Nitration of Toluene (Oxidation Method).*

(4, i) *Oxidations.*—Since the principal aim of this group of experiments was to estimate the percentage of *m*- and *o*- plus *p*-isomerides to an accuracy approaching ± 0·1%, it was necessary to establish a method of oxidation which should be non-selective to within ± 2%. The mixture of nitro-compounds was boiled with 100 parts of water in a large flask, the well-ground condenser of which supported at its upper end a small gas-washing flask containing a little acetone. A small excess of potassium permanganate solution (3%) was added little by little over a period of 12 hours, the additions being timed to keep pace with the decolorisation. The acetone was returned to the flask, and the heating continued with further additions of permanganate for 6 hours, after which the solution was completely decolorised by adding alcohol, and filtered. The oxides of manganese were extracted thrice by treatment with steam, and the combined filtrates and washings were acidified whilst hot, basified with ammonia, and treated with a few c.c. of calcium chloride solution. The next day the solution was filtered, and the combined filtrate and washings were made alkaline with potassium hydroxide, evaporated to a small bulk, acidified, and extracted 6 times with pure ether.

Pure *o*-, *m*-, and *p*-nitrotoluene were separately oxidised in this way. The acids obtained on removal of ether and drying in a vacuum had m. p.'s 3—5° below those of the pure compounds, and this necessitated the procedure referred to in Section (4, ii). Several mixtures of isomerides were treated in the same way. The yields, given in Table VIII, show that the condition of non-selectivity is fulfilled to the necessary degree of approximation.

TABLE VIII (Expts. 81—90).

Oxidised	*o*-	*m*-	*p*-	*o*- + *p*-	*m*-
Yield (%)	78·4	79·0	80·6	78·5	81·0
Oxidised	*m*-	*p*-	*o*-	*o*- + *m*-	*m*- + *p*-
Yield (%)	82·2	80·6	80·1	80·9	81·6

(4, ii) *Solubility Determinations.*—The method used was that of Holleman (*Rec. trav. chim.*, 1899, **18**, 268), but, since the nitrobenzoic acids obtained by oxidation are not quite pure, as is shown by the m. p.'s of the acids derived from pure nitrotoluene (Section 4, i), Baker's procedure (J., 1927, 568) was followed for eliminating error due to small amounts of acid impurities.

Several flasks, each containing the same known volume (V c.c.) of solutions saturated at 25° with respect to both *o*- and *p*-nitrobenzoic acids, together with crystals of both acids, were closed with accurately fitting ground-glass stoppers bearing thin films of grease on the ground surfaces, and rotated in a thermostat at 25°. To each flask, except the first, a weighed sample of mixed nitrobenzoic acids had been added containing insufficient *m*-isomeride to saturate the liquid; and, after 24 hours, equal samples (v c.c.) of the solutions were withdrawn through a filter for titration (titres $t_1 \ldots t_n \ldots$ c.c.). To each flask, including the first, pure *m*-nitrobenzoic acid was now added in quantity more than sufficient to saturate the liquid; and, after rotation in the thermostat for another 24 hours, samples of the same volume (v c.c.) were again withdrawn and titrated (titres $t'_1 \ldots t'_n \ldots$ c.c.). The alkali was approximately $0{\cdot}01N$-barium hydroxide, and, if 1 c.c. of this is equivalent to z mg. of nitrobenzoic acid, the number of mg. of meta-acid contained in the sample added to the nth flask is given by the formula

$$(t_n - t_1)\frac{V}{v}z - (t'_n - t'_1)\left(\frac{V}{v} - 1\right)z$$

the second term of which represents the correction for the acid impurities introduced during oxidation. The volumes V and v were 75·06 c.c. and 10·00 c.c. throughout.

Correction is necessary also for the circumstance that the isomeric nitrobenzoic acids affect each other's solubility. This was applied on the basis of data obtained by carrying through the preceding process as far as the first series of titrations with different quantities of pure *m*-nitrobenzoic acid as the added samples. By comparing the weights calculated from the expression $(t_n - t_1)Vz/v$ with those added, the differences shown in Table IX were obtained, and from the smoothed curve of these the correction figures, given in the lower part of the table, can be read.

TABLE IX (Expts. 91—99).

Added (mg.)	7·1	19·6	25·9	35·2	44·8
Found (mg.)	6·1	18·0	24·6	34·5	45·0
Difference	+1·0	+1·6	+1·3	+0·7	−0·2
Apparent *m*- (mg.) ...	10	20	20	25	30
Correction (mg.)	+1·3	+1·5	+1·4	+1·3	+1·1
Added (mg.)	51·0	54·6	58·2	64·7	
Found (mg.)	51·2	55·6	59·8	67·9	
Difference	−0·2	−1·0	−1·6	−3·2	
Apparent *m*- (mg.) ...	40	50	60	70	
Correction (mg.)	+0·3	−0·6	−1·9	−3·5	

(4, iii) *Error of Analysis.*—As the above method has never previously been used to obtain percentages as small as those of the proportion of the *m*-nitration product of toluene, it was tested by application to artificial mixtures containing the isomeric nitrotoluenes in approximately the proportions in which they are formed in nitration. The results are in Table X.

In Expt. 101 the addition of calcium chloride to the oxidation solution was omitted, and, probably for this reason, the titre difference representing foreign acids (row 9) bears an unusually high ratio to the main titre difference (row 8). The corrections applied in row 12 are taken from Table IX.

TABLE X.

Expt. No.		101	102	103	104	105
Nitro-toluenes	ortho (%) ...	59·4	58·7	58·0	56·2	61·4
	meta (%) ...	3·0	4·0	5·2	4·5	2·6
	para (%) ...	37·6	37·3	36·8	39·3	36·0
Oxidation yield (%)		76·6	77·9	80·8	77·6	79·1
Acids analysed (mg.)		834·2	627·9	532·5	830·0	815·2
Baryta (z in mg.)		1·782	1·782	1·782	1·822	1·822
$(t_n - t_1)V/v$ (c.c.)		19·6	15·8	16·8	22·6	16·1
$(t'_n - t'_1)(V - v)/v$ (c.c.)		6·1	2·0	1·8	3·6	3·0
Difference (c.c.)		13·5	13·8	15·0	19·0	13·1
Meta, found (uncorr.) (mg.)		24·5	24·6	26·7	34·7	23·9
,, ,, (corr.) (mg.)		25·8	26·9	28·0	35·4	25·2
Percentage meta		3·1	4·1	5·3	4·3	3·1
Error		+0·1	+0·1	+0·1	−0·2	+0·5

(4, iv) *Results.*—Nitrations nos. 111—119 were carried out with 1·0 g.-mol. of toluene, and 0·25—0·5 g.-mol. of acetyl nitrate, with or without an excess of acetic anhydride as is shown in col. 2 of Table XI, the third col. of which indicates the temperature of nitration. The products of Expts. 112—114 and 118—120 were distilled to constant density (Section 2, ii), and those of Expts. 111 and 115—117 were completely distilled once under the conditions of distillation to constant density. The yields of acids obtained by oxidation are in col. 4, and an indication of their purity is given by the figures in cols. 7 and 8, from which the acid value of the impurities relatively to that of the meta-acid can be deduced. Cols. 5—8 contain the observational data from which the percentages of meta-compound (col. 9) are calculated.

TABLE XI.

Expt. No.	Excess Ac_2O (g.-mols.).	Temp.	Oxidation yield (%).	Acids analysed (mg.).	Baryta z (mg.).	$\frac{t_n - t_1}{v/V}$ (c.c.).	$\frac{t'_n - t'_1}{v/(V-v)}$ (c.c.).	Meta, % (corr.).
111	0·0	0°	81·6	827·5	1·822	17·4	2·6	3·4
112	1·0		78·8	762·7	1·822	17·1	2·3	3·6
113	1·0		76·8	842·1	1·822	17·8	2·4	3·4
114	1·0		79·9	836·0	1·822	18·4	2·1	3·6
						Mean meta-content =		3·5
115	0·0	30°	76·0	764·3	1·822	17·1	1·9	3·7
116	0·0		79·9	840·0	1·869	20·9	3·6	3·9
117	0·0		80·7	832·7	1·869	25·5	5·7	4·6
118	1·0		80·0	743·6	1·822	17·5	2·7	4·2
119	1·0		77·4	845·7	1·869	21·5	4·1	3·9
120	1·0		78·4	800·5	1·869	24·3	3·7	4·8
						Mean meta-content =		4·2

(5) *Proportions of Isomerides formed in Nitration of Toluene (Freezing-point Method).*

(5, i) *Method.*—Holleman's method (*Rec. trav. chim.*, 1914, **33**, 1) was used, but we interpreted our ternary freezing-point diagram without assuming empirical relations between the depressing effect of added *m*-nitrotoluene on the f. p.'s of pure and mixed *o*- and *p*-isomerides, and this necessitated a detailed study of the small region of the diagram required. Advantage was taken of the dimorphism of *o*-nitrotoluene to obtain in all cases two " second freezing points," and hence two sets of values for the percentage composition of the mixtures.

The f. p.'s were measured by the cooling-curve method, with the usual precautions against too great supercooling and too rapid heat-transfer. They are uncorrected, but were all measured under standardised conditions with the same thermometer. Dewar vessels were used, and (except at the moments when the liquid was being inoculated) atmospheric moisture was excluded.

(5, ii) *Freezing Points of Artificial Mixtures.*—The first three columns of Table XII show the compositions. The figures in the col. headed γ are " first freezing points," in which the solid phase is *p*-nitrotoluene; those under the heading β are "second freezing points" in which the β-modification of *o*-nitrotoluene accompanies the *p*-isomeride in the solid phase; and those under the heading α are "second freezing points" in which *p*-nitrotoluene and the α-modification of *o*-nitrotoluene together constitute the solid phase. Individual f.-p. readings were read to 0·05°, and each recorded f. p. is the mean of several such readings (usually three).

TABLE XII.

Expt. No.	Composition (%).			Freezing points.		
	Ortho-.	Meta-.	Para-.	γ.	β.	α.
121	61·47	0·00	38·53	+2·73°	−15·25°	−21·00°
122	59·60	3·15	37·25	+1·03	−17·05	−22·55
123	58·92	4·32	36·76	+0·65	−17·70	−23·20
124	58·13	5·58	36·29	−0·02	−18·47	−23·77
125	59·31	0·00	40·69	+5·03	−15·23	−20·87
126	56·65	4·47	38·88	+2·95	−17·85	−23·45
127	57·23	0·00	42·77	+7·50	−15·10	−21·10
128	55·68	2·86	41·46	+6·00	−16·95	−22·27
129	55·03	3·92	41·05	+5·43	−17·45	−23·00
130	54·30	5·20	40·50	+4·80	−18·23	−23·63

(5, iii) *Freezing-point Surfaces.*—Within the limited range of compositions to which the data of the preceding section relate, the three sets of f. p.'s lie on plane surfaces to a sufficient degree of approximation. The introduction of quadratic terms was tried, but did not noticeably improve the general consistency of the results.

The following mean planes are adopted:

$$\begin{aligned}\gamma &= 71{\cdot}55 - 112\,\omega - 115\,\mu\\ \beta &= -13{\cdot}11 - 3{\cdot}5\,\omega - 61\,\mu\\ \alpha &= -22{\cdot}53 + 2{\cdot}5\,\omega - 47{\cdot}5\,\mu\end{aligned}$$

Here, $100\,\omega$ and $100\,\mu$ respectively represent the percentages of the ortho- and the meta-isomeride, and γ, β, and α correspond with the headings of Table XII (explained in Section 5, ii). The freezing points calculated from these equations to correspond with the compositions of the mixtures used in Expts. 121—130 are shown in Table XIII, together with the deviations of the observations from these calculated values. Only 5 of the 30 deviations fall outside ± 0·1° and these appear to be casual in sign and distribution.

(5, iv) *Freezing Points of Nitration Products.*—These are in Table XIV, the 2nd, 3rd, and 4th cols. of which indicate the conditions of nitration (1 g.-mol. of toluene was used throughout). The products of Expts. 132, 133, and 136—139 were distilled to constant density, whilst those of Expts. 131, 134, and 135 were distilled to the correct density although its constancy was not, in these cases, proved by a further distillation. The f. p.'s contained in cols. 5—7 are each a mean of several independent readings.

TABLE XIII.

Compositions as in	Calculated f. p.'s and deviations.					
Expt. No.	γ.	$\Delta\gamma$.	β.	$\Delta\beta$.	α.	$\Delta\alpha$.
121	+2·70°	+0·03°	−15·26°	+0·01°	−20·99°	−0·01°
122	+1·18	−0·15	−17·12	+0·07	−22·53	−0·02
123	+0·60	+0·05	−17·80	+0·10	−23·11	−0·09
124	+0·03	−0·05	−18·55	+0·08	−23·72	−0·05
125	+5·12	−0·09	−15·19	−0·04	−21·05	+0·18
126	+2·96	−0·01	−17·81	−0·04	−23·24	−0·21
127	+7·45	+0·05	−15·21	+0·02	−21·10	±0·00
128	+5·90	+0·10	−16·81	−0·14	−22·49	+0·22
129	+5·41	+0·02	−17·43	−0·02	−23·01	+0·01
130	+4·75	+0·05	−18·18	−0·05	−23·63	±0·00

TABLE XIV.

Expt.		Free Ac_2O		Freezing points.		
No.	Reagent.	(g.-mols.).	Temp.	γ.	β.	α.
131	$AcNO_3$	0·00	0°	+2·70°	−17·30°	−22·80°
132	,,	1·00	0	+2·55	−17·47	−22·95
133	,,	1·00	0	+2·40	−17·40	−22·90
134	,,	0·00	30	+1·30	−17·83	−23·30
135	,,	0·00	30	+1·50	−17·77	−23·30
136	,,	1·00	30	+1·05	−17·80	−23·30
137	,,	1·00	30	+0·80	−17·90	−23·45
		$MeNO_2$ (g.-mols.).				
138	HNO_3	1·00	30	+1·03	−17·77	−23·10
139	,,	2·00	30	+0·90	−18·02	−23·13

(5, v) *Proportions of Isomerides.*—The equations for γ, β, and α (Section 5, iii) might theoretically be used in pairs, but the $\alpha\beta$-pair is obviously useless for the evaluation of ω, and of little worth for determining μ, owing to the small differences (6 and 13·5, respectively) between the coefficients of these variables. We have therefore used the $\beta\gamma$-pair and the $\alpha\gamma$-pair to obtain two sets of values for the composition. The pairs of equations used are indicated by the Greek letters in the headings of cols. 3—8 of Table XV, which also shows the calculated compositions, and the mean values of these, for the nitrating agents and nitration temperatures indicated in col. 2. The general agreement with Holleman's results (*loc. cit.*) is satisfactory.

(6) *Summary of Data.*

(6, i) *Ratio of Velocities of Nitration of Benzene and Toluene.*—The mean values for $100k_x/(k_x + k_y)$ obtained from Tables IV and VII are assembled in Table XVI. The figures for the most thoroughly studied set of nitration conditions (nitration by acetyl nitrate at 30°) show a discrepancy of 0·5 between the results yielded by the two methods of analysis. The numerous checks carried out on these make it difficult to ascribe the difference to any known fault of analytical procedure, and its cause may therefore be sought in

TABLE XV.

No.	Conditions.	Ortho. $\beta\gamma$.	Ortho. $\alpha\beta$.	Meta. $\beta\gamma$.	Meta. $\alpha\beta$.	Para. $\beta\gamma$.	Para. $\alpha\beta$.
		Percentage compositions.					
131	$AcNO_3$ in Ac_2O at 0°	58·0	57·8	3·6	3·6	38·4	38·6
132		58·1	57·8	3·9	3·9	38·0	38·3
133		58·4	58·0	3·8	3·9	37·8	38·1
Means		58·2	57·9	3·8	3·8	38·0	38·3
134	$AcNO_3$ in Ac_2O at 30°	58·4	57·9	4·5	4·7	37·1	37·4
135		58·3	57·8	4·3	4·6	37·4	37·6
136		58·7	58·8	4·3	4·7	37·0	36·5
137		58·8	57·9	4·5	5·0	36·7	37·1
Means		58·5	58·1	4·4	4·7	37·1	37·2
138	HNO_3 in $MeNO_2$ at 30°	58·8	58·1	4·3	4·3	36·9	37·6
139		58·4	58·9	4·7	4·3	36·9	36·8
Means		58·6	58·5	4·5	4·3	36·9	37·2

some constant error attending the nitrations. It has been noted that the results are expected to be extremely sensitive to traces of rapidly nitrating impurities in the toluene, and a possible cause of the discrepancy is the not quite complete removal of such impurities from the toluene by the partial freezing to which it was subjected. This suggestion receives support from some special experiments showing that when unpurified toluene was used, the results exhibited much larger (about four-fold) discrepancies in the same direction; but the means of these diverse results, obtained by the two methods, approximate to the values we obtain using purified toluene. This suggests that the means of final results obtained by the density and the reduction methods will represent more probable values than either set of data taken separately, and these means (for nitration with acetyl nitrate) are given in Table XVI, col. 4. Col. 5 contains the corresponding values for the reduced velocity of nitration of toluene (k_y/k_x) under the three sets of nitration conditions investigated; the figure for nitration with acetyl nitrate at 30° should be tolerably accurate, but it must be remembered that the other values depend on much smaller numbers of experiments, and that the second significant figures, shown in italics, are therefore of doubtful accuracy.

TABLE XVI.

Conditions of nitrations.	$100k_x/(k_x + k_y)$. Method. Density.	Reduction.	Mean.	$\frac{k_{\text{toluene}}}{k_{\text{benzene}}}$.
$AcNO_3$ at 0°	3·7	3·5	3·6	2*7*
,, at 30°	4·45	3·95	4·2	23
HNO_3 at 30°	4·5	—	4·5	2*1*

(6, ii) *Proportions of Isomerides formed in Nitration of Toluene.*—The mean values, obtained by oxidation, by freezing point in conjunction with the eutectic surface given by the β-modification of the ortho-compound, and by freezing point in conjunction with the surface corresponding to the α-modification of the ortho-compound, for the three sets of nitration conditions studied, are assembled in Table XVII. The finally adopted mean values, also given in the table, are in some cases arbitrarily modified by not more than 0·1% to make the various groups of percentage figures total 100·0.

TABLE XVII.

Nitrotoluene.	Analytical method.	Nitration conditions.		
		$AcNO_3$ at 0°.	$AcNO_3$ at 30°.	HNO_3 at 30°.
Ortho	F. p., β-surface	58·2	58·5	58·6
	,, α-surface	57·9	58·1	58·5
	Mean	58·1	58·4	58·5
Meta	Oxidation	3·5	4·2	—
	F. p., β-surface	3·8	4·4	4·5
	,, α-surface	3·8	4·7	4·3
	Mean	3·7	4·4	4·4
Para	F. p., β-surface	38·0	37·1	36·9
	,, α-surface	38·3	37·2	37·2
	Mean	38·2	37·2	37·1

(6, iii) *Coefficients of Activation for Toluene.*—These are calculated from the data in Tables XVI and XVII by using the formulæ

$$F_{\text{ortho}} = 3\omega k_y/k_x,\ F_{\text{meta}} = 3\mu k_y/k_x,\ F_{\text{para}} = 6\pi k_y/k_x$$

where 100 ω, 100 μ, and 100 π represent the percentages of simultaneously formed *o*-, *m*-, and *p*-nitrotoluenes, and k_y/k_x is the reduced velocity of nitration of toluene. The values of F for the various nitration conditions studied, together with those of the derived quantity $\Delta E = RT.\log_e F$, are given in Table XVIII, where those significant figures which at present are of doubtful value are shown in italics.

TABLE XVIII.

Nitration conditions.	*F.*			ΔE (Cals.).		
	Ortho.	Meta.	Para.	Ortho.	Meta.	Para.
$AcNO_3$ at 0°	4*7*	3·*0*	6*2*	2·1*0*	0·6*0*	2·2*4*
,, at 30° ...	40	3·0	51	2·21	0·66	2·36
HNO_3 at 30°	3*7*	2·*8*	4*7*	2·1*7*	0·6*2*	2·3*0*

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