CCCLXXXI.—*The Ionisation of Aromatic Nitro-compounds in Liquid Ammonia. Part II.*

By WILLIAM EDWARD GARNER and HENRY FRANK GILLBE.

THE aromatic dinitro-compounds undergo ionisation in liquid ammonia at measurable speeds (Part I, Field, Garner, and Smith, J., 1925, **127**, 1227), giving rise to solutions the molecular conductivities of which are comparable in magnitude with those of typical electrolytes in this solvent. At moderately high dilutions, the ionisation is nearly complete. The rates of ionisation of the *m*-derivatives, as determined by conductivity measurements, are in agreement with the equation for reactions of the first order, whereas those of the *o*- and *p*-derivatives change in accordance with the equation for reactions of zero order. The *m*-compounds become faintly coloured immediately after solution, and blue or purple when the ionisation has reached its equilibrium value : the *o*- and *p*-derivatives are colourless initially and yellow or brown at the end of the ionisation. These colour changes are of interest in that they accompany changes in conductivity and hence may be due to the production of ions. If the ions only are coloured, then it should be possible by measurements of the extinction coefficients of the solutions to determine their concentration and to examine the relationship between ionic concentration and conductivity.

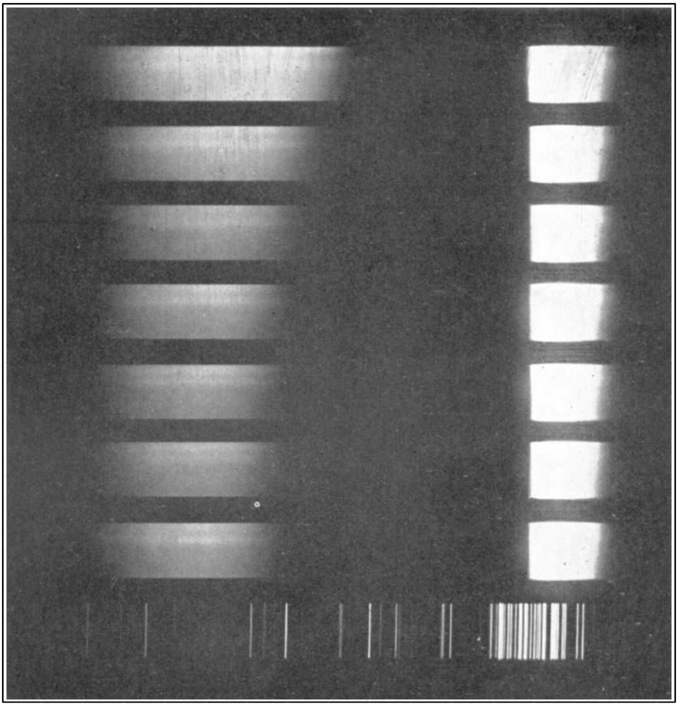
The absorption spectra of the *m*-dinitro-compounds show two bands, one in the yellow and one in the near ultra-violet, both increasing in width as the ionisation proceeds. In the case of the first band, this increase is due mainly to a movement of the less refracted edge. This is seen in photographs (Fig. 1) of the absorption spectra of solutions of *m*-dinitrobenzene taken at various times after the preparation of the solution. The neon spectrum photographed on the same plate provides a means of measuring the change in the width of the adsorption bands with time. A simple relationship holds between the wave-length of the edge of this band and the conductivity, *viz.*, $(\lambda_0 - \lambda_t)/\mu_t =$ constant, where λ_0 and λ_t are the wave-lengths (in Å.U.) of the edge of the band at the commencement of ionisation and at time t (in mins.), respectively, and μ_t is the product of specific conductivity (in mhos) and dilution at time t (see Table I). The dilution was in all cases 416·2 litres, and the values of the specific conductivity are taken from the previous paper (*loc. cit.*).

TABLE I.

	m-Dinitrobenzene. $\lambda_0 = 4891$.				2 : 4-Dinitrotoluene. $\lambda_0 = 5490$.		
t.	μ_t.	λ_t.	$(\lambda_0 - \lambda_t)/\mu_t$.	t.	μ_t.	λ_t.	$(\lambda_0 - \lambda_t)/\mu_t$.
10	96·8	4592	3·09	66	71·9	5116	5·20
13	109	4559	3·04	71	75·6	5100	5·15
17	118	4527	3·08	95	89·0	5035	5·12
20	123	4512	3·08	134	104·6	4948	5·17
24	126	4500	3·10	190	118·0	4868	5·27
29	130	4497	3·03	254	126·0	4826	5·26
36	131	4496	3·01	303	130·0	4806	5·25
	3 : 4-Dinitrotoluene. $\lambda_0 = 4160$.				3 : 5-Dinitrotoluene. $\lambda_0 = 5000$.		
72	1·55	4515	229	16	52·8	4731	5·10
84	1·72	4552	228	20	55·7	4716	5·10
116	2·18	4674	235	25	58·8	4702	5·07
160	2·81	4815	233	32	61·5	4689	5·05
217	3·63	4995	230	42	62·8	4680	5·10

The above relationship between the change in the wave-length of the edge of the absorption band and the conductivity is readily understood if both of these properties are directly proportional to the concentration of the ions. The movement of the edge of the band with change in concentration is not necessarily linear in character; the nature of the relationship depends on the type of photographic plate used and its sensitivity to light of different wave-lengths. The constancy of $(\lambda_0 - \lambda_t)/\mu_t$ is therefore very largely fortuitous. It does suggest, however, that both $\lambda_0 - \lambda_t$ and

FIG. 1.



Neon.

[To face p. 2890.

μ_t are very possibly directly proportional to the concentration of a coloured ion. In order to settle this point definitely, it is necessary to make measurements of the extinction coefficients of monochromatic radiation passing through the solution. These have now been made at constant temperature (at or near $-35°$) for a number of wave-lengths with *m*-dinitrobenzene, and at one wave-length for 2 : 4-dinitrotoluene.

The extinction coefficient E may be defined by the equation $I/I_0 = e^{-Ecd}$, and if Beer's law be assumed to hold for these solutions, from one value of c and measurements of I/I_0 over a period of time, the change in concentration of the coloured substance can be followed. Such measurements are now described (see Experimental).

For this series of experiments, the concentrations of nitro-compounds were chosen in the region where ionisation is practically complete (94—96%), and hence the final ionic concentration will be the same as the initial concentration of the nitro-compound. The concentrations (c, in mols./l.) of the coloured substance calculated from this value and from measurements of I/I_0 are given in Table II. The ratio of conductivity l_t to c_t is constant. The conductivities of the solutions were measured between two platinum electrodes, and, in the case of 2 : 4-dinitrotoluene, simultaneously with the measurements of extinction coefficients. The cell constant was not

TABLE II.

m-Dinitrobenzene.

$v = 5880$; temp. $= -34{\cdot}5°$.

t.	$10^7 . c_t$.*	v.	l_t.	$l_t/c_t . 10^{-4}$.
3	974	10,270	875	899
6	1301	7,690	1128	867
9	1445	6,920	1310	907
15	1587	6,300	1498	944
20	1638	6,110	1545	944
25	1660	6,020	1560	939
30	1682	5,950	1570	934

* Mean of values at 4340 and 4192 Å.

2 : 4-Dinitrotoluene.

$v = 4170$; temp. $= -34°$; $\lambda = 4650$ Å.

t.	$10^7 . c_t$.	l_t.	$l_t/c_t . 10^{-5}$.
20	520	1082	208
40	876	1756	200
60	1236	2590	209
90	1436	3072	214
120	1820	3612	198
150	2040	4012	197
190	2140	4430	207
230	2268	4784	211
270	2240	4896	219
300	2330	5050	217

$v = 4340$; temp. $= -35{\cdot}1°$; $\lambda = 4650$ Å.

t.	$10^7 . c_t$.	l_t.	$l_t/c_t . 10^{-5}$.
20	407	985	242
40	773	1810	234
90	1342	3284	245
120	1534	3842	250
150	1748	4270	244
190	1919	4656	243
230	2064	5050	245
270	2110	5242	248

measured, hence the values for the conductivity are given in arbitrary units.

The concentration of the coloured substance as determined from the extinction coefficients is directly proportional to the conductivity of the solution at all stages during the process of ionisation. The colour of the solutions of *m*-dinitro-compounds is therefore due to the ions and not to any other substances formed during the ionisation; thus, the rate of production of the coloured ions in these compounds obeys the equation for reactions of the first order.

The ions present in these solutions were shown previously to be the nitro-compound in the form of an anion, and positively charged ammonia molecules as kations. Since the colour varies from one nitro-compound to another, the coloured ion must be the anion.

Nature of the Ionisation in Solutions of Nitro-compounds in Liquid Ammonia.

The majority of substances dissolved by liquid ammonia obey the law of mass action in their ionisation much better than those in aqueous solutions. The law of mass action holds fairly accurately for dilute solutions of liquid ammonia (Kraus, "Properties of Electrically Conducting Systems," p. 56). On applying the equations $K_1 = \alpha^2/v(1 - \alpha)$ and $K_2 = \alpha^3/v^2(1 - \alpha)$ to Franklin's values of the molecular conductivity of *m*-dinitrobenzene in liquid ammonia, it is found that K_1 gives a much better constant than K_2 (Table III).

TABLE III.

v.	μ.	K_1.	$K_2 \times 10^4$.	v.	μ.	K_1.	$K_2 \times 10^4$.
12·38	45·7	0·0044	0·74	188·4	106·0	0·0024	0·06
24·42	53·35	0·0032	0·32	380·0	131·7	0·0024	0·04
43·30	71·5	0·0036	0·27	752·0	156·4	0·0023	0·02
95·40	90·2	0·0030	0·13	1485·0	179·9	0·0024	0·01

The dissociation constant K_1 is very similar to that of typical binary salts in ammonia; *e.g.*, for ammonium chloride, $K = 0{\cdot}0016$; for potassium bromide, $K = 0{\cdot}0022$; and for potassium nitrate, $K = 0{\cdot}0017$ (Franklin and Kraus, *Amer. Chem. J.*, 1900, **23**, 298). The evidence is thus in favour of the view that the ionisation of dinitro-compounds in liquid ammonia is of a binary character.

It was shown previously that one of the ions was in all probability NH_3^{++} (or $N_2H_6^{++}$), since no trace of any substance was detectable at the cathode either during or after electrolysis of a solution of *m*-dinitrobenzene in ammonia. Hence it was suggested that the ionisation process was

$$R(NO_2)_2 + NH_3 \overset{(I)}{\rightleftharpoons} R(NO_2)_2,NH_3 \overset{(II)}{\rightleftharpoons} R(NO_2)_2^{--} + NH_3^{++} \quad (1)$$

On the basis of the Lewis–Langmuir octet theory, it is more probable that the ammonia ion is $N_2H_6^{++}$, and that the equation should be

$$R(NO_2)_2 + 2NH_3 \overset{(I)}{\rightleftharpoons} R(NO_2)_2,2NH_3 \overset{(II)}{\rightleftharpoons} R(NO_2)_2^{--} + N_2H_6^{++} \quad (2)$$

Attempts were made to prepare the intermediate compound, $R(NO_2)_2,2NH_3$, which might be stable in the solid state. A vapour-pressure method was used at temperatures in the neighbourhood of —40°, but no evidence was obtained for the existence of such a compound. It is, however, necessary to assume the formation of an intermediate compound during the ionisation process, otherwise it is impossible to explain the fact that the rate of ionisation of 2 : 6-dinitrotoluene, which is only ionised to the extent of about 2% at 400 litres, obeys the first-order law. Equation (3) is therefore unlikely :

$$R(NO_2)_2 + 2NH_3 \rightleftharpoons R(NO_2)_2^{--} + N_2H_6^{++} \quad . \quad (3)$$

If this equation represented the course of the reaction, the occurrence of the preponderating reverse reaction would prevent a constant being obtained for the equation $k = 1/t \,.\, \log_e a/(a - x)$.

This applies to a less degree also to the other dinitro-compounds, which are not completely ionised at dilutions of 400 litres (compare Part I, *loc. cit.*). Thus, we are driven to the conclusion that the stage in the reaction which determines the order is not the ionisation process, and therefore we postulate the formation of an intermediate compound [stage (I), reaction (2)].* Whatever the nature of this reaction, since it obeys the first-order law, it must go to completion.

In the previous paper, the equation

$$k = 1/t \,.\, \log_e \mu_e/(\mu_e - \mu_t) \quad . \quad . \quad . \quad . \quad (4)$$

where μ_e and μ_t are the molecular conductivities of the solutions at the end of the reaction and at a time *t*, respectively, was applied to the changes in conductivity in solutions of nitro-compounds. This equation is only strictly accurate, when applied to reaction (2), if the dilutions are such that the ionisation is complete. When the ionisation is incomplete, the conductivity is no longer an exact measure of the amount of intermediate compound produced, and equation (4) requires modification. If α_e and α_t represent the degrees of ionisation at equilibrium and at a time *t*, respectively, then the equation

$$k = \frac{1}{t} \log_e \frac{\mu_e/\alpha_e}{\mu_e/\alpha_e - \mu_t/\alpha_t} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

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* The critical increment of the reaction, which is found to be 7,520 calories, is that corresponding to chemical change rather than to an ionisation process, for which a much larger value is probable.

would be expected to be more nearly correct than equation (4). The values of α may be obtained from the specific conductivities of Franklin by plotting κ against α. Table IV shows the effect of applying equation (5) to the velocity measurements for *m*-dinitrobenzene.

TABLE IV.

t.	μ.	κ.	a.	μ/a.	k.	k (Part I).
10	84·3	0·404	0·556	152	0·107	0·140
12	89·4	0·429	0·542	165	0·105	0·133
16	98·3	0·471	0·520	189	0·109	0·131
22	106·0	0·508	0·500	212	0·114	0·133
10	96·8	0·232	0·687	141	0·109	0·132
13	109	0·262	0·660	165	0·116	0·134
17	118	0·283	0·645	183	0·115	0·132
22	123	0·296	0·635	194	0·112	0·134
24	126	0·302	0·630	200	0·117	0·129

For those nitro-compounds which are ionised considerably in liquid ammonia, the use of equation (5) does not improve the constancy of k. There is, however, an appreciable source of error in interpolating from Franklin's results. In the case of 2 : 6-dinitrobenzene, where the ionisation is much less complete, there is a marked improvement in constancy. To make this calculation, it is assumed that the conductivity at infinite dilution is the same for 2 : 6-dinitrotoluene as for *m*-dinitrobenzene. Such an assumption is justifiable, since the introduction of a methyl group into a heavy aromatic molecule would have but little effect on the mobility of the anion. The following results are thus obtained :

t	11	54	108	162
k	0·015	0·015	0·014	0·015
k (Part I)	0·028	0·021	0·017	0·015

The very feebly ionised 2 : 6-dinitrotoluene gives a good constant when k is calculated from equation (5). The assumptions made above with respect to the mechanism of the ionisation process have been justified by all of the facts at our disposal.

The values of k calculated from the measurements at higher dilutions, $v = 4000$, where α does not change appreciably during the reaction, agree within experimental error (see results for 2 : 4-dinitrotoluene, Table VII).

Thus equation (2) represents in a satisfactory manner the course of the reaction. The first stage is a slow reaction which goes to completion, and the second stage is rapid and proceeds to equilibrium. At moderate concentrations, the ionisation is not complete. The characteristic colour of these solutions is due to the anion, which is very probably $R(NO_2)_2^{--}$. There is a direct proportionality between the conductivity of the solutions and the concentration of the anion at any time during the course of the reaction.

EXPERIMENTAL.

Preliminary Absorption Measurements.—A simple form of apparatus was used consisting of a light-tight wooden box with a tightly fitting lid; at one end was fixed a 250-c.p. Pointolite lamp, and at the other an unsilvered Dewar vessel of about 280 c.c. capacity, which could be wedged tightly against a hole of about 2 cm. diameter at the end of the box. The light passing through the Dewar vessel fell on the slit of a Hilger constant-deviation spectrometer.

The Dewar vessel was nearly filled with liquid ammonia, and a known amount of nitro-compound added, either as a solid or in solution in 1 or 2 c.c. of ethyl alcohol. Photographs were taken after varying intervals of time on the same plate (Fig. 1). The addition of the nitro-compounds in solution ensured a greater rapidity of admixture, and the presence of a small quantity of alcohol did not affect the rate of ionisation. With the slit at 0·15 mm., and with Ilford Panchromatic plates, an exposure of $\frac{1}{2}$—1 minute was found to be ample for the dilutions used. For ease in determining the edges of the absorption bands, a neon spectrum was photographed above and usually below each series of spectra.

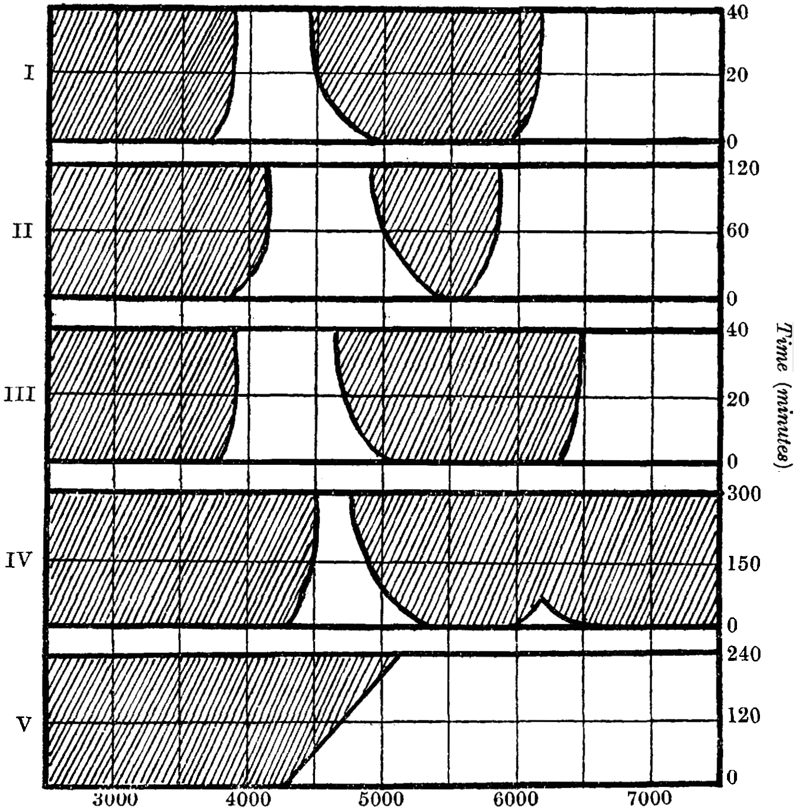
Although the plates were panchromatic, the intensity of the image obtained with the light passing through liquid ammonia alone was not quite uniform from one end of the spectrum to the other, especially in the green. The image was, however, sufficiently uniform for the purpose of the above measurements, since the movement of the edge of the bands occurred over a narrow region of the spectrum.

Experiments were made with *m*-dinitrobenzene and 2 : 4-, 2 : 6-, 3 : 5-, and 3 : 4-dinitrotoluenes at a dilution of 416·2 litres. The position of the absorption bands and the movement of the absorption edges with time are given in Fig. 2. The shaded regions show the absorption bands.

One or two points of interest emerge from the spectrum–time diagrams (Fig. 2). All the *m*-dinitrotoluenes and *m*-dinitrobenzene show absorption bands at about 3000—4000 Å. In all cases the bands widen with time. The introduction of a methyl group in the meta-position to two nitro-groups (I and III) has hardly any effect either on the position or on the velocity of movement of the edge of the bands. If this group is ortho to one of the nitro-groups (IV), the band in the yellow narrows; and if it is ortho to two nitro-groups (II), the band is narrower still. Nitro-groups ortho or meta to a methyl group have but little effect on the position of the ultra-violet band, whereas the introduction of a *p*-nitro-group (IV) shifts this edge towards the red and also causes the appearance of an absorption band in the extreme red. The absorption edge of 3 : 4-dinitrotoluene moves linearly with time.

Molecular Compounds.—It was considered possible that compounds of the type $R(NO_2)_2,xNH_3$ might be stable in the solid state, especially as the solids separating on evaporation of the ammonia solutions appeared to be coloured. Vapour-pressure measurements made on solutions of both the *m*- and the *o*- and *p*-derivatives during the process of evaporation failed to yield any evidence of the occurrence of such compounds in the solid state. A range of temperatures down to —48° was covered.

FIG. 2.



Wave-length, Å.U.

I. m-*Dinitrobenzene.* II. 2 : 6-*Dinitrotoluene.* III. 3 : 5-*Dinitrotoluene.* IV. 2 : 4-*Dinitrotoluene.* V. 3 : 4-*Dinitrotoluene.*

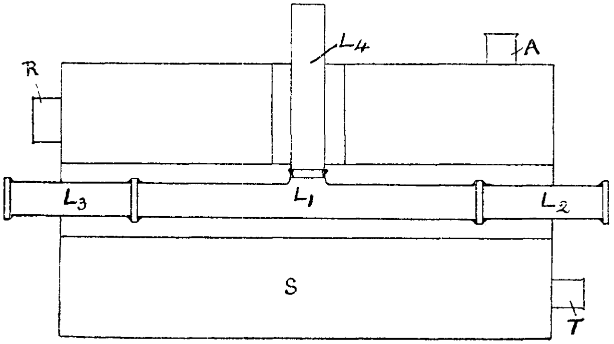
Critical Increment of Reaction.—From conductivity measurements of solutions of *m*-dinitrobenzene in liquid ammonia over a range of temperatures, the critical increment of the reaction was shown to be 7,520 cal. The corresponding velocity coefficients were :

Temp.	$-34{\cdot}4°$	$-39{\cdot}3°$	$-41{\cdot}3°$	$-44{\cdot}5°$
k	0·176	0·133	0·116	0·087

The wave-length corresponding to the energy of activation lies in the infra-red at 3·78 μ. The change was not accelerated by the light from a mercury-vapour lamp.

Measurement of Extinction Coefficients.—To make measurements of extinction coefficients, it was necessary to enclose a known volume of solution in a vessel maintained at constant temperature and having optically worked windows at a known distance apart. The final form of the apparatus is shown in Fig. 3. The constant-temperature bath consisted of a welded, mild-steel tank, S, measuring about 6″ × 4″ × 4″, filled with commercial ammonia; R is an opening for a temperature regulator and air vent, T an opening for an alcohol thermometer, and A the air inlet. The temperature was controlled by regulating a stream of air, bubbling through the ammonia, by means of a relay and magnetic cut-off. The thermostat was heavily lagged with felt.

FIG. 3.



The reaction vessel consisted of four parts, L_4 fitting into L_1 by means of a ground joint, and the end portions L_2 and L_3 being attached to L_1 by means of guttapercha and separated by polarimeter plates. L_2 and L_3 projected some distance beyond the ends of the tank and their end plates prevented condensation of water vapour on the ends of L_1 during the measurements. Guttapercha was found to be the only suitable cement at —35° for attaching the polarimeter plates; other adhesives either cracked at the low temperature or were attacked by liquid ammonia.

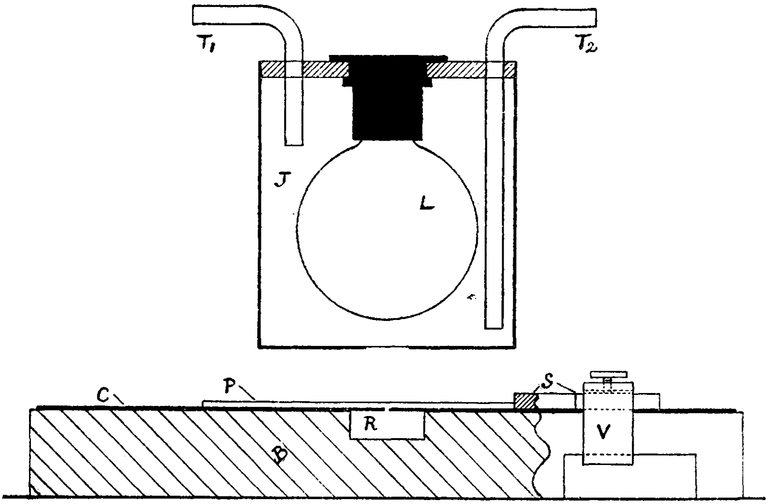
The tank was placed in position between a Hilger constant-deviation spectrograph and a light-tight wooden box containing a Pointolite lamp and a condensing lens system. The current through the lamp was maintained constant to 1 part in 500 parts. The width of slit found to be most satisfactory was 0·15 mm.

The experimental procedure was as follows : (1) The tank was filled with commercial ammonia and the temperature adjusted to the required value. (2) The reaction tube was filled with pure ammonia. (3) A trial exposure was made in order to ensure that there was even illumination along the length of the collimator slit : it was impossible to determine this visually. (4) A series of photographs was taken with exposures varying from 5 seconds to 1 minute of that part of the spectrum at which it was intended to make measurements, with a neon spectrum above and below the series. During this operation the rest of the plate was screened with a thin piece of cardboard. (5) The dark slide was moved a certain distance horizontally, and the card screen removed. (6) A known volume of an alcoholic solution of the dinitro-compound under investigation was added to the reaction tube and the volume made up immediately to a mark on the vertical tube, L_4. At this moment a stop-watch was started, and the first exposure made as soon as possible. A series of photographs was then taken over the whole period of the reaction—about 30 minutes in the case of *m*-dinitrobenzene—an exposure of 1 minute being given in each case. As only 6 or 7 photographs could be taken on one plate, the earlier ones were taken at shorter intervals than those at the end of the reaction, since at the beginning the spectrum was changing most rapidly. Photographs were therefore taken at about 2, 5, 9, 14, 19, 24, and 30 minutes from the commencement of the reaction. (7) Photographs of the neon spectrum were taken immediately above and below the reaction exposures.

It was intended to make simultaneous measurements of the conductivities of the solutions, but owing to the short time taken for the reaction to go to completion, this was not always possible. The final experiments were made with 2 : 4-dinitrotoluene, which takes some 5—6 hours to attain equilibrium. In this instance, conductivity measurements could without difficulty be made simultaneously with the photographs of the absorption spectra. In other cases, conductivity measurements were made separately.

Measurement of the Plates.—The densities of the photographic images were measured by means of a thermopile connected to a Moll galvanometer with the usual lamp and scale. The apparatus constructed for this purpose is shown in Fig. 4. The thermopile (not shown) was fixed rigidly in the recess, *R*, in the wooden block, *B*, the leads being taken out through the sides of the block. Attached to the surface of the block was a sheet of blackened card, *C*, having a slit immediately above the thermopile element about 1 mm. wide and somewhat shorter than the width of one of the spectral images on the photographic plate. At a short distance above the slit was clamped a "Fullolite" lamp, *L*, surrounded by a blackened glass tank, *J*, having a clear circle at the bottom. A rapid stream of water at constant temperature could be circulated through the tank *via* the tubes T_1 and T_2. This ensured the removal of infra-red radiation from the beam which reached the thermopile; errors would otherwise have been introduced by the gradual heating of the apparatus, and by variations in the thickness of the glass plate, since glass shows marked absorption in the infra-red.

FIG. 4.



It was necessary to ensure that the same wave-length band would be measured for each of the spectra of a series, *i.e.*, that the movement of the plate necessary to bring successive spectra of a series over the slit was in a direction at right angles to the length of the spectra. This was accomplished by preparing a number of steel strips with accurately parallel edges and of known width, from about $\frac{1}{8}''$ to $2''$ wide. A steel straight edge was clamped to the block *B* in such a position that when the plate to be measured was moved with one edge always in contact with the straight edge, corresponding lines in the two neon spectra could be superimposed in succession on the slit above the thermopile element. Measurements of the spectral images at the wave-length of this line could thus be carried out. By placing between the straight edge and the edge of the plate one or more of the steel strips, further series of measurements at other wave-lengths could be made. In the figure, two of the steel strips are shown held in position by the clamp, *V*. *P* represents a plate in position for measurement.

Knowing the rate of change of wave-length along the neon spectrum, together with the width of the steel strips used, the wave-lengths at which the measurements had been made could be calculated. Measurements were made at the same wave-lengths for the calibration exposures as for the exposures made during the reaction. In all cases the galvanometer deflexions were taken as the plate was moved backwards and forwards above the slit.

Having measured the densities of the images given by the calibration exposures and by the "reaction exposures" (at the same wave-lengths), one can calculate the fraction of light transmitted through the solution at any time. In the calculation which follows, it is assumed that the density of the image is directly proportional to the total quantity of light energy falling on the plate, an assumption which, although not rigidly true, is approximately so over a certain range of exposures [compare Baly, *Proc. Roy. Soc.*, 1927, *A*, **113**, 711, for a critical investigation of the Schwarzschild equation, $D = kIT^n$; the statement is there made that the results "would seem definitely to establish that the Schwarzschild exponent (n) is unity"]. In all the measurements with *m*-dinitrobenzene, the calibration curves obtained by plotting time of exposure against galvanometer deflexion are straight lines over the range employed in the further calculation.

In Table V are given the calibration figures for Plates I and II, for *m*-dinitrobenzene; *T* is the time of exposure in seconds, and under the various wave-lengths are given the galvanometer deflexions for each image. *A* is the intercept of the calibration line on the deflexion axis, and $b/60$ the slope of the line (in secs./cm.) divided by 60, a quantity which is required in the subsequent calculation of the extinction coefficients.

TABLE V.

	Plate I.				Plate II.		
T.	Deflexions at λ (Å.U.).				Deflexions at λ (Å.U.).		
	4340.	4192.	4560.	4140.	4340.	4192.	4560.
5	169	177	50	209	276	201	144
10	151	157	37	187	254	181	127
15	130	136	26	168	—	—	—
20	114	122	15	146	217	144	96
25	92	100	6	125	194	126	80
30	76	84	4	111	180	114	61
35	60	74	3	106	166	109	47
40	—	—	—	—	162	106	32
$A =$	188	196	62	230	296	220	162
$b/60 \times 10^6 =$	4387	4387	6945	3970	4167	4386	5051

Let D = density of image, I = intensity of light falling on the photographic plate, and d = galvanometer deflexion due to the image. Then, for the calibration exposures

$$D_n = kT_nI_0 = k'(A - d_n) \quad . \quad . \quad . \quad . \quad (6)$$

since on plotting T against d for the calibration exposures a straight line is obtained; n refers to the number of seconds. In this case I_0 is constant and T variable.

For the " reaction exposures " $D_t = kT_0I_t$, where T_0 is constant (= 60 secs.), and I_t, the intensity of light transmitted by the solution at time t, varies as the reaction proceeds. Further, we may write

$$D_t = k'(A - d_t) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where A is the deflexion for the plate when exposed to light of zero intensity, and is necessarily the same as in equation (6).

The quantity required is I_t/I_0, the fraction of the incident light transmitted through the solution at time t. From equations (6) and (7)

$$\frac{I_t}{I_0} = \frac{(A - d_t)T_n}{(A - d_n)T_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

But $T_n/(A - d_n)$ is the slope of the line obtained by plotting T against d for the calibration exposures, in sec./cm. Putting this equal to b, and substituting for T_0 = 60 secs., we have

$$I_t/I_0 = b(A - d_t)/60 \quad . \quad . \quad . \quad . \quad . \quad (9)$$

The extinction coefficient is defined by E in the equation

$$I = I_0e^{-Ecd'} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where I/I_0 is the fraction of light transmitted through a layer of solution of thickness d' and concentration c.

If it be assumed that the reaction between the dinitro-compound and ammonia goes to completion, the concentration at equilibrium will be the concentration of the nitro-compound added initially, and the value of E can be calculated by taking the extrapolated value of I/I_0 at equilibrium, and substituting the necessary values in equation (10). The figures obtained for E are given in Table VI.

The extinction coefficient E being known, the change in concentration of the absorbing substance can be determined by transforming equation (10) thus

$$c = -(1/Ed') . \log I/I_0 \quad . \quad . \quad . \quad . \quad . \quad (11)$$

and this gives the values of c appearing in Table VI (cols. 3 and 6).

By substituting the calculated values of c in the unimolecular formula

$$k = 1/t . \log_e (c_0 - c_e)/(c_t - c_e) \quad . \quad . \quad . \quad (12)$$

where c_0 is the initial, and c_e the equilibrium concentration, and c_t the concentration at time t, we obtain a similar velocity coefficient to that resulting from the conductivity measurements (see Table VI, cols. 4 and 7). The high initial values of k are probably due to difficulties in mixing, but any error in the zero time would affect measurements of extinction coefficients and of conductivity equally.

By interpolating values of the specific conductivity at the same temperature and times as the calculated concentrations, the molecular conductivities can be calculated. These are summarised in Table II: v is the dilution, l_t the interpolated specific conductivity, and in the last column is given a value proportional to molecular conductivity, which is practically constant over the range of dilutions concerned. Franklin (*Z. physikal. Chem.*, 1909, **69**, 272) finds a change of only about 2% over this range of dilutions, which is less than the experimental error.

Results.

The thickness of the solution was in all cases 3·83 cm., being the length of the middle portion L_1 of the reaction tube (Fig. 3). The concentrations given in Tables VI and VII are in g.-mols. per litre, and the galvanometer deflexions, d, in mm.

(1) m-*Dinitrobenzene* (*Plates I and II*).—The alcoholic solution contained 0·1 g. of *m*-dinitrobenzene in 100 c.c.; 0·1 c.c. of this solution was added from a pipette to the reaction vessel, the volume of which was 3·50 c.c. Since the molecular weight of *m*-dinitrobenzene is 168, the dilution of the ammonia solution was 5880 litres. In Tables VI and VII are given the results at a number of wavelengths. For the extinction coefficient measurements, t is the mean time of the exposure; when conductivity measurements were made simultaneously, the figure given is for a time mid-way between the beginning and the end of the exposure.

In a further experiment at − 38° (Plate II) similar values of k were obtained. These are not given, since there are no data for the specific conductivity of *m*-dinitrobenzene at this temperature.

(2) 2 : 4-*Dinitrotoluene*.—The change in the intensity of the light falling on the plate was much greater than in the experiments with *m*-dinitrobenzene, since the reaction was followed over a greater range of concentrations. The range of exposures was so great that the Schwarzschild relation, $D = k\ I\ T$, no longer held. It was therefore necessary to employ another method of calibrating the photographic plate. Dilute aqueous solutions of permanganate of known concentrations (less than $M/1000$) were placed in the cell, and used to determine the manner in which the intensity on the photographic plate varied with the concentration of the solution in

the path of the light. This method when employed for *m*-dinitrobenzene gave results almost identical with those obtained by the first method.

TABLE VI.

Plate I. *m*-Dinitrobenzene. Temp. = – 34·5°.

t (mins.).	d_t.	$10^7 . c_t$.	k.	d_t.	$10^7 . c_t$.	k.
3	81	978	0·286	12	847	0·230
6	104	1291	0·237	30	1205	0·205
9	112	1420	0·200	35	1340	0·173
15	121	1583	0·180	40	1505	0·145
20	124	1642	0·168	43	1622	0·154
25	125	1663	0·147	44	1665	0·154
30	126	1683	0·154	44	1665	0·129
	$\lambda = 4340$; $E = 202$.			$\lambda = 4560$; $E = 326$.		
3	109	971	0·283	134	1072	0·333
6	134	1312	0·246	158	1388	0·283
9	143	1471	0·223	164	1488	0·230
15	149	1591	0·184	168	1557	0·166
20	151	1635	0·163	171	1613	0·150
25	152	1658	0·147	173	1651	0·143
30	153	1682	0·152	174	1671	0·136
	$\lambda = 4192$; $E = 259$.			$\lambda = 4140$; $E = 235$.		

TABLE VII.

2 : 4-Dinitrotoluene.

Temp. = – 34°; v = 4170; λ = 4650 Å.			Temp. = – 35·1°; v = 4340; λ = 4650 Å.		
t.	$c_t . 10^7$.	k.	t.	$c_t . 10^7$.	k.
20	520	0·0122	20	407	0·0097
40	876	0·0113	40	773	0·0102
60	1236	0·0120	90	1342	0·0097
90	1436	0·0101	120	1534	0·0092
120	1820	0·0117	150	1748	0·0095
150	2040	0·0127	190	1919	0·0093
190	2140	0·0117	230	2064	0·0098
230	2268	0·0126	270	2110	0·0092
270	2240	0·0101			
300	2330	0·0150			

Summary.

The velocity of the process of ionisation of solutions of *m*-dinitro-compounds in liquid ammonia obeys a first-order law, even in those cases where the ionisation does not proceed to completion. Measurements of the change in conductivity and extinction coefficients of solutions of *m*-dinitro-compounds in liquid ammonia have shown that the ionic concentration at any time is proportional to the conductivity. The coloured ion in these solutions is an organic anion.

The most probable course of the reaction is

$$R(NO_2)_2 + 2NH_3 \overset{(I)}{\rightleftharpoons} R(NO_2)_2,2NH_3 \overset{(II)}{\rightleftharpoons} R(NO_2)_2^{--} + (N_2H_6)^{++},$$

the velocity of the reaction being governed by (I), which proceeds to completion. The process of ionisation is very probably instantaneous.

The temperature coefficient is that of ordinary chemical reactions, *i.e.*, the velocity doubles for 10° rise of temperature; the critical increment is about 7520 cal.

No evidence has been obtained for the existence in the solid state of complexes such as $R(NO_2)_2,xNH_3$.

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