TRANSFORMATION OF DIAZOCYANIDES

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ABSTRACT. The rate of spontaneous transformation of *cis-p*-chlorobenzenediazocyanide into the *trans*-isomeride has been followed in benzene and carbon tetrachloride solutions by means of the change in dielectric constant. The half life period thus found appears to be independent of the initial concentrations and therefore the change is of the first order.

From the measurement of the velocity constants of the transformation carried out at different temperatures the energy of activation is calculated to be about 23 kg.-cals. in either benzene or carbon tetrachloride solution.

The geometric isomerism of the *cis-trans* type in nitrogen compounds was first suggested by Hantzsch and Werner in 1890 when it was shown that certain oximes are capable of being transformed to the more stable isomeride under certain conditions. The concept was subsequently extended to doubly linked nitrogen compounds, notably to certain phenylhydrazones and diazo-compounds and from various experiments which since followed it can now be said with a fair degree of certainty that the low melting form of the diazocyanides, the form that is initially produced, is the *cis* and that the high-melting or stable form is the *trans*.

Labile form	Stable form
Ar—N	Ar—N
‖	‖
X—N	N—X
cis	*trans*
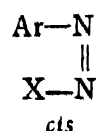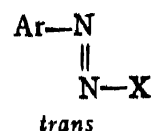
For various controversies extending over years leading to the establishment of these structures the following references may be seen : Hantzsch and Reddelien (1923), Hantzsch (1894), Hantzsch and Schulze (1895), Hantzsch (1895), Euler and Hantzsch (1901), Gabriel (1879), Hantzsch and Danziger (1897), Hantzsch and Schultze (1895b), Stephenson and Waters (1939), and Le Fèvre and Vine (1938).

When the constitutions of the diazocyanides were fairly established by all available chemical means, Hantzsch and Danziger (1897) prepared nearly twenty diazocyanides in their isomeric forms. Both isomerides were orange yellow in colour and sparingly soluble in water but gave solutions in non-polar solvents in which they were soluble. The labile form has always the lower melting point, greater solubility and couples much more easily in alcoholic solutions with β-naphthol. Hantzsch and co-workers could not determine the rate, order, etc., of this transformation owing to the difficulty in following this type of change by chemical means and to the imperfections of the physical methods of following this type of change.

In the present work an attempt has been made to follow this spontaneous isomerisation in different non-polar solvents by means of dielectric constant

change, transformation of
$$
\begin{array}{ccc}
\text{Ar—N} & & \text{Ar—N} \\
\| & \longrightarrow & \| \\
\text{X—N} & & \text{N—X}
\end{array}
$$
being associated with a change

of capacity of a condenser having
$$
\begin{array}{c}
\text{Ar—N} \\
\| \\
\text{X—N}
\end{array}
$$
molecules as part of the dielectric.

There are a number of difficulties for the systematic study of the *cis* ⟶ *trans* transformation of benzenediazocyanides. The unsubstituted benzenediazocyanide $C_6H_5.N=N.CN$ is difficult to obtain in the pure form and doubt has been expressed whether it exists as $C_6H_5.N=N.CN$ or as $C_6H_5.N=N.CN$, HCN (Hantzsch, 1900) (Hantzsch and Schulze, 1895c). An attempt was made to prepare this substance by treating the diazotised solution of aniline with potassium cyanide in the usual way and an oily liquid was separated which was found to be highly unstable and explosive. Its benzene solution, however, showed a change of dielectric constant with time showing that the isomerisation was taking place.

Most *cis*-benzenediazocyanides are either unstable and easily isomerisable or stable and very slowly isomerisable, and in the latter case require a higher temperature for their study. These substituted benzenediazocyanides which isomerise very easily such as *p*-nitrobenzenediazocyanide are not very suitable for measurement at widely separated temperatures. On the other hand, *p*-bromobenzenediazocyanide is stable and moderately easily isomerisable so that inconveniently high temperatures are necessary to study the temperature coefficient. The variation of the dielectric constant of a non-polar liquid is not linear with temperature beyond a certain range. Besides, the high temperature introduces certain other errors connected with the experimental cell and the apparatus. Another difficulty is that the solutions of *cis*-benzenediazocyanides lose nitrogen at high temperatures. For these reasons measurements have been confined to the temperature range of 25°C and 35°C. A list of some of the very well-known *cis*-diazocyanides is given in the Table I, with their nature and characteristics. *cis*-*p*-chlorobenzenediazocyanide is seen to be stable and easily isomerisable, and the transformation to the *trans*-isomer can be obtained within moderate temperature.

TABLE I

p-Nitro-	*cis*-benzenediazocyanide	...	Unstable, very easily isomerisable.
p-Chloro-	,,	,,	...	Stable, easily isomerisable.
p-Bromo-	,,	,,	...	Stable, moderately easily isomerisable.
o-Bromo-	,,	,,	...	Very stable, difficultly isomerisable.
m-Bromo-	,,	,,	...	Unstable, not isomerisable.
2 : 6-Dibromo-	,,	,	...	Very unstable, not directly isomerisable.
2 : 5 ⎫ 3 : 4 ⎬-Dibromo- 3 : 5 ⎭	,,	,,	...	Stable, slowly, spontaneonsly isomerisable.
2 : 4- ,,	,,	,,	...	Very stable, not spontaneonsly isomerisable.
2 : 4 : 6-Tribromo-	,,	,,	...	Very stable, difficultly isomerisable.
2 : 4 : 6-Trichloro-	,,	,,	...	Very stable, difficultly isomerisable.
2 : 4 : 5-Trichloro-	,,	,,	...	Stable, easily isomerisable.

For those compounds which are difficultly isomerisable, their minimum temperature of isomerisation may be as high as 100°C and usual solvents such as benzene, carbon tetrachloride, etc., cannot be employed conveniently. The *cis*-form of *p*-chlorobenzenediazocyanide having a melting point of 29°C, is easily purified and convenient to handle. It was therefore chosen as the representative of the aryl-diazocyanides.

The solutions of the *cis*-diazocyanides are liable to change completely to the stable *trans*-diazocyanides or to decompose with evolution of nitrogen or hydrocyanic acid, according to the nature of the solvent and temperature used. Thus in ether solution side-reactions may occur along with the usual isomerisation, whilst in alcohol and acetone solutions *cis*-diazocyanides rapidly darken and gradually evolve nitrogen to the extent of 20%-40% of the total quantity of the diazo-group present. The isomerisation of the *cis* to the *trans*-diazocyanides is quantitative only in non-ionising solvents such as benzene and carbon tetrachloride (Stephenson and Waters, 1939). It is because of these reasons that benzene and carbon tetrachloride have been used as solvents. The choice of the benzenediazocyanides, solvents and temperatures are severely limited for a dynamic study such as that contemplated.

The recorded procedure (Hantzsch and Schutze, 1895*a*; Hantzsch and Danziger, 1897) was followed with particular modifications regarding purification and drying. *p*-Chloroaniline (0.1 g.-mol.) was dissolved in concentrated hydrochloric acid (0.45 g.-mol. or 45 c.c.) and water (45 c.c.) and diazotised with sodium nitrite (0.1 g.-mol.) with constant cooling and shaking. The resultant diazotised mixture was filtered and cooled to −10°C in solid carbon dioxide and acetone mixture, 50 c.c. of absolute alcohol being added in order to prevent the mixture from freezing. Potassium cyanide (0.2 g.-mol. or 13 g.) in water (25 c.c.) was added slowly with constant stirring so that the final mixture remained acid to litmus. The yellow precipitate was filtered off under suction, washed with chlorine-free, ice-cold water, dried as far as possible under suction, and then dissolved in cold, light petroleum with a little ether. The mixture was then shaken for ten minutes with anhydrous sodium sulphate, filtered and well-cooled in solid carbon dioxide-acetone mixture, when the labile *p*-chlorobenzene-diazocyanide was deposited. The solid was washed with a little cold light petroleum and dried by evaporating off the solvent in a current of dry air.

It has been observed by the author that a dry specimen of labile *p*-chloro-benzenediazocyanide can be kept for some time in a vacuum desiccator in a refrigerator without appreciable change.

The apparatus used in determining the dielectric constant is shown diagrammatically in Fig. 1. The component parts are as follows: Q, Hilger quartz crystal (circular, 857 kilocycles per second), V_1, Valve (Mullard PM 12), V_2, Valve (Mullard PM 202), L_1, Inductance (diameter 3″ approx. with 40 turns of wire), L_2, Inductance (diameter 2·5″ approx. with 34 turns of wire), C_1 and C_2, Fixed condensers (2μF each), C_3, Variable condenser (maximum 250 $\mu\mu$F), C_4, Experimental cell (80 $\mu\mu$F with air dielectric), C_5, Fixed variable condenser (maximum

1200 $\mu\mu$F), C_n, Standard variable condenser, Sullivan type (maximum 30 $\mu\mu$F), R, Resistance (1 megohm), M Milliammeter (0 – 5 milliamps.), G, Galvanometer (Moll type, 4 volts on magnet) and B, Grid bias battery.
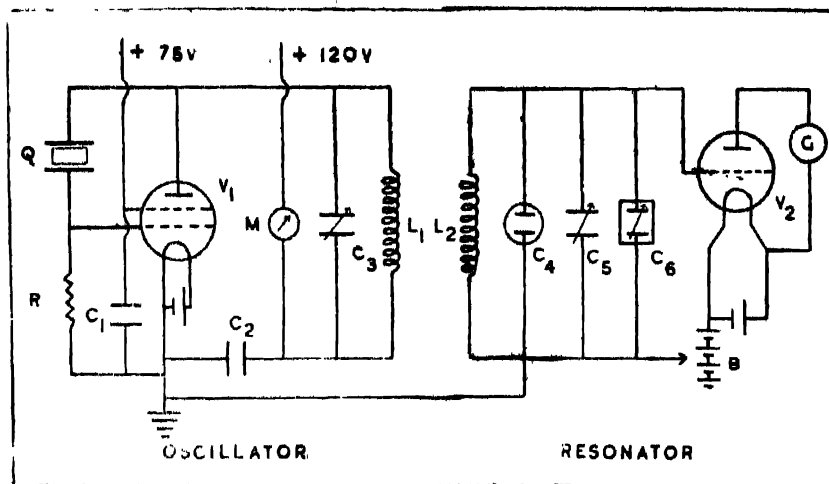
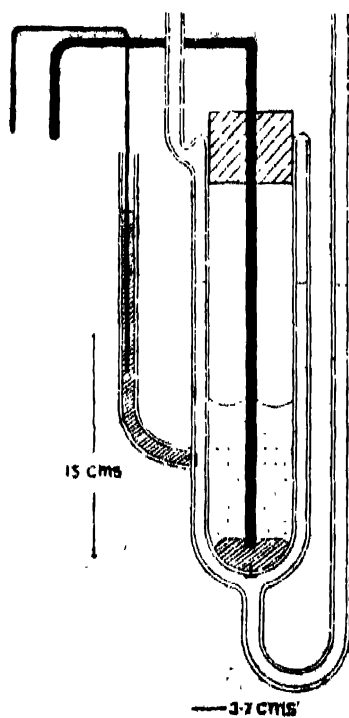Apparatus for measuring dielectric constant

FIG. 1

Perhaps a word is necessary about the experimental cell C_4. It has therefore been shown in great detail in the adjoining sketch, Fig. 2. It is of modified Sayce and Briscoe type (Sayce and Briscoe, 1925). It consists of two concentric glass tubes similar to boiling tubes, the outer surface of the inner tube and the inner surface of the outer tube, i.e., the internal surfaces of the annular space of the tubes, are coated with colloidal graphite films to form the plates of the condenser. The outer surface of the inner tube formed the high potential plate and the inner surface of the outer tube was connected to the earth and was therefore the low potential plate.

FIG. 2

The dielectric constants of solutions of *p*-chlorobenzenediazocyanides in benzene for different weight fractions as the transformation proceeds are graphically represented in Fig. 3. The half life periods have been shown by arrows and are practically identical within the experimental error. The change is therefore a monomolecular one. The following table summarises the half life periods for benzene and carbon tetrachloride solutions at different temperatures.
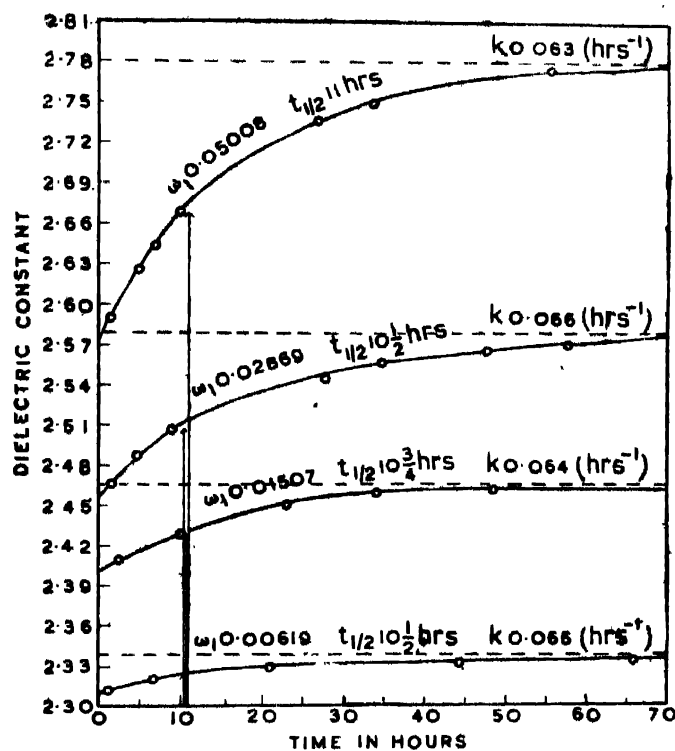
INFLUENCE OF CONCENTRATION ON ISOMERISATION
OF p-chloro-benzene diazocyanide
IN BENZENE SOLUTION AT 25°C.

FIG. 3

TABLE II

Solvents	Weight fraction	Temp.	Time of half change	$k = \dfrac{2.303 \log_2}{t_{\frac{1}{2}}}$	$\log_{10} k$ (hrs^{-1})	$1000/T$
Benzene	0·05008	25°C	11 hrs.	0.06294	−1.2010	3.356
,,	0.02461	30°C	6½ hrs.	0·10670	−0.9720	3.301
,,	0.03234	35°C	3½ hrs.	0.19810	−0.7032	3.246
Carbon tetrachloride	0 01637	25°C	16 hrs.	0.04333	−1.3632	3.356
,,	0.01513	30°C	8 hrs.	0.08666	−1.0622	3.301
,,	0·01457	35°C	4½ hrs.	0.15400	−0.8123	3.246
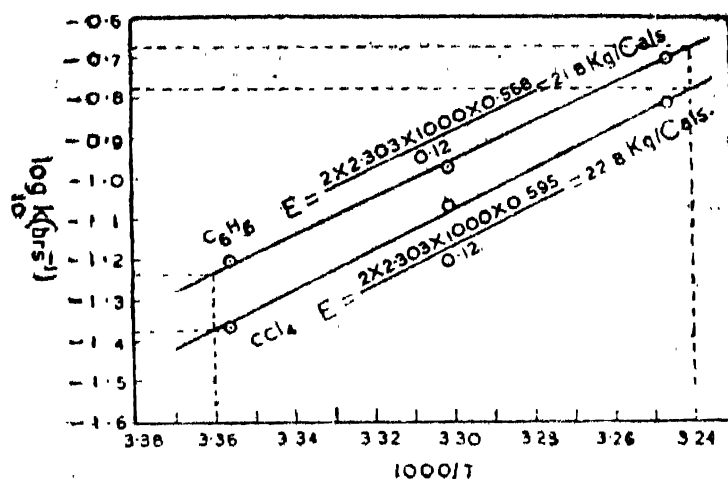
Influence of temperature and solvents on transformation of
p-chloro-benzene diazocyanide

FIG. 4

Log k (hrs^{-1}) is shown against $1000/T$ multiple of reciprocal absolute temperature in the adjoining graph (Fig. 4). This bears a linear relation. The conversion therefore follows a first order equation in both solvents. As calculated

from the equation $E = \dfrac{R \log_e (k_1/k_2)}{1/T_2 - 1/T_1}$, derived from the Arrhenius equation

$k = Ae^{E/RT}$, the slopes of the lines give a mean activation energy of about 22 kg.-cals./g.-mol. for the change in benzene solution and 23 kg.-cals./g.-mol. in carbon tetrachloride solution which may be taken as identical within the experimental error and do not require a different mechanism in the two solvents.

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