# **348.** *Thermal Isomerisation of Potassium* p-*Sulphonyloxybenzenediazoate in Concentrated Alkali.*

By R. J. W. Le Fèvre and R. Roper.

An attempt is made to measure, by a spectrophotometric method, the kinetics of a true normal to iso-diazoate transformation free from side reactions. For the normal sodium diazoate from sulphanilic acid the rate constants at 49·7° agree with those found by Le Fèvre and Sousa, but at 29·7° they are somewhat greater. Support is provided for the previous contention that the isodiazoate from sulphanilic acid is extensively hydrolysed in dilute alkali to the isodiazohydroxide.

Le Fèvre and Sousa [1] examined the kinetics of thermal isomerisation of the normal diazoate of sulphanilic acid in 0·5—4·85N-sodium hydroxide and discussed and reviewed the ready decomposition of most normal diazoates. They concluded that the decomposition (*i.e.*, diazo-resin formation and nitrogen loss) of alkaline solutions of the normal diazoate is negligible and that thermal isomerisation to the isodiazoate is 97—100% complete with all strengths of alkali used. This conclusion depends, however, on the quantitative coupling of aliquot parts of the reaction mixture with slightly alkaline β-naphthol solutions at the commencement and at the close of the experiment. Since the coupling reaction is known to proceed through the diazonium ion,[2] it is now submitted that the reaction actually measured was the " loss of diazonium ion " (or of normal diazoate, since the two are in equilibrium) and did not differentiate between actual decomposition and thermal isomerisation to the isodiazoate. Essentially the same reaction has also been measured by Brown, Duffin, Maynard, and Ridd [3] for solutions of lower pH, but without comment on the nature of the products.

Loss of nitrogen from diazonium salts in acid solution was found by De Tar and Ballentine [4] to give first-order rate constants of 13—25 × $10^{-5}$ sec.$^{-1}$, with Arrhenius parameters, $E$, of 25—29 kcal. mole$^{-1}$ and log $A$ values of 15—16. Le Fèvre and Sousa's parameters for decomposition of diazosulphanilic acid in alkaline solutions are $E$ = 25—26 kcal. mole$^{-1}$ and log $A$ = 13·3—13·9. For reactions which are known to be true thermal geometrical isomerisations about N=N bonds values of $E$ between 21—28 and of log $A$ between 10 and 15 have been collected.[1] The Arrhenius parameters, therefore, do not decide between the different reaction possibilities.

It is the purpose of the present paper to examine the changes of the normal diazoate spectrophotometrically and to measure kinetics for a true normal to iso transformation free from side reactions. For reasons outlined below the reaction was followed in

---

[1] Le Fèvre and Sousa, *J.*, 1955, 3154.

[2] Saunders, " The Aromatic Diazo-compounds and their Technical Applications," Arnold, London, 2nd edn., 1949; Wittwer and Zollinger, *Helv. Chim. Acta*, 1954, **37**, 1954; Zollinger, *ibid.*, 1953, **36**, 1273.

[3] Brown, Duffin, Maynard, and Ridd, *J.*, 1953, 3937.

[4] De Tar and Ballentine, *J. Amer. Chem. Soc.*, 1956, **78**, 3916.

concentrated alkali. In an earlier paper[5] we have shown that the isodiazoate from sulphanilic acid is extensively hydrolysed to the isodiazohydroxide in 0·1N-sodium hydroxide. Support for this comes from the present kinetics for which it will be shown that reasonable rate constants cannot be obtained if the isodiazoate anion is assumed to be the predominant diazo-species in dilute alkali. The spectral behaviour of isodiazoates in concentrated alkali has been discussed qualitatively for several diazoates.[5]

*Spectral Changes Accompanying Isomerisation.*—Spectra for the isomeric diazoates from sulphanilic acid have been reported for solutions in water and 0·1N-sodium hydroxide. To examine the course of the thermal reaction, solutions of the normal diazoate in 0·1N- and 1·3N-sodium hydroxide were kept in the spectrophotometer at 25° and the changes in absorption spectra were recorded. Different behaviour was observed for the dilute and the concentrated solutions (see Figs. 1 and 2).

The absorption by normal diazoate in 0·1N-sodium hydroxide (curve 1, Fig. 1) increases with time at $\lambda > 244$ mμ and decreases for lower wavelengths. Two absorption maxima develop at about the same rate: one at 280 mμ corresponding to the formation of the isodiazo-species and the other at 256 mμ, which, by comparison with the spectrum of an authentic sample, corresponds to the formation of *p*-sulphonyloxyphenoxide ion. Since both normal and iso-diazo-spectra show strong absorption at low wavelengths, the rapid decrease in absorbance below the isosbestic point at 244 mμ represents rapid loss of the diazo-component.

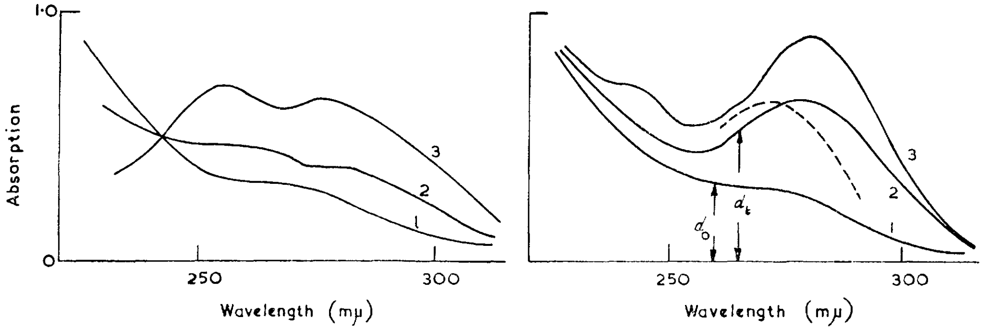

FIG. 1. FIG. 2.

Spectral changes in (FIG. 1) 0·1N-NaOH and (FIG. 2) 8·3N-NaOH. In Fig. 2, the broken curve is calculated for a mixture of normal and iso-diazoate in 0·1N-NaOH.

For solutions of the normal diazoate in 8·3N-sodium hydroxide (Fig. 2) the absorption increases with time over the whole wavelength range (220—320 mμ). The increase in absorbance is greatest between 270 and 280 mμ and a single peak develops (curve 2) corresponding to the formation of isodiazo-species. Only after several hours can phenoxide formation be detected by the presence of a peak at 256 mμ (curve 3). The continued strong absorption at *ca.* 220 mμ shows the retention of most of the diazo-material. With continued storage the 280 mμ isodiazo-peak attains a maximal value while the phenoxide continues to increase slowly. The early part of the reaction is thus almost entirely the thermal isomerisation of the normal to isodiazo-species and therefore is used in the subsequent section to determine kinetics of this transformation.

For solutions of normal diazoate in 8·3N-sodium hydroxide, but at higher temperatures, the formation of phenoxide becomes evident much sooner than at 25°, and ultimately proceeds to a much greater extent than at this temperature.

## EXPERIMENTAL

*Calculation of Rate Constants.*—Referring to Fig. 2, let $d_0$ and $d_t$ be the absorbances at the commencement of the isomerisation and at time $t$, respectively, for a selected wavelength, and

---

[5] Le Fèvre, Roper, and Reece, *J.*, 1959, 4104.

$E_n$ and $E_i$ be molar extinction coefficients at this wavelength for the normal and isodiazo-component, respectively. It is required to introduce these quantities into the standard kinetic equation for a first-order reaction,

$$\log_{10} a/(a - x) = k_i t/2{\cdot}303, \qquad \text{(i)}$$

where $k_i$ is the first-order rate constant, $a$ is the concentration of normal diazoate at time 0 [*i.e.*, $a = (n - D)_{t=0}$] and $x$ is the concentration of isodiazo-species at time $t$ [*i.e.*, $x = (i - D)_t$]. Assuming the Beer–Lambert laws and for a cell path length $l$ cm. we have

$$a = (n - D)_{t=0} = d_o/(l\,.\,E_n). \qquad \text{(ii)}$$

If the molar extinction coefficients are additive for mixed solutions, then at time $t$, the absorbance $d_t$ has a contribution, $d_n'$ from the normal diazotate ion, and a contribution, $d_i'$ from the isodiazo-species:

*i.e.*,

$$\begin{aligned} d_t &= d_i' + d_n' \\ &= E_i l(i - D)_t + [d_o/E_n l - (i - D)_t]E_n l \end{aligned}$$

On rearrangement this gives

$$x = [i - D]_t = (d_t = d_o)/l(E_i - E_n). \qquad \text{(iii)}$$

Inclusion of equation (ii) and (iii) reduces equation (i) to:

$$\log_{10} \frac{(E_i - E_n)}{E_i - E_n d_t/d_o} = \frac{tk_1}{2{\cdot}303}. \qquad \text{(iv)}$$

Thus for a plot of $\log_{10} (E_i - E_n)/(E_i - E_n d_t/d_o)$ against $t$ a straight-line plot passing through the origin should be obtained, and from this $k_1 = 2{\cdot}303 \times$ Slope.

*Measurement of Rate Constants.*—The kinetic experiments were carried out in a temperature-controlled cell by the Spectracord instrument. Temperatures recorded are those of the reacting solutions after equilibration.

Since the precise concentration of the diazoate solution need not be known, 1 drop of a freshly prepared stock solution of diazosulphanilic acid in 0·1N-hydrochloric acid was introduced into a 2-cm. quartz cell containing 8·3N-sodium hydroxide at the reaction temperature. An appropriate reference solution was used and the spectrum of the reactants was recorded immediately after mixing (*ca.* 1 min.). Zero time was taken as the time of entry into the cell and $d_o$ was obtained by extrapolation to zero time of the absorbance $d_t$ for the first 5 min. The spectrum was recorded at intervals for the remainder of the kinetic run or until decomposition was evident.

For a particular wavelength, with values of $E_i$ and $E_n$ as previously determined for solutions in 0·1N-sodium hydroxide,[5] and the experimental $d_o$ and $d_t$, the results were plotted in terms of equation (iv). Straight-line plots through the origin were obtained and values of $k_1$ calculated from the slope.

*Results.*—First-order rate constants of the right order of magnitude were obtained, but were markedly dependent on the wavelength of measurement. With longer wavelengths, $k_1$ increased as shown by the following representative run at 29·7°:

| $\lambda$ (m$\mu$) | 260 | 268 | 280 | 290 | 300 | 310 |
|---|---|---|---|---|---|---|
| $10^5 k_1$ (sec.$^{-1}$) | 0·88 | 0·97 | 1·15 | 1·29 | 1·42 | 1·64 |

The values used for $E_i$ in calculating rate constants were those found for a solution of the isodiazoate in 0·1N-sodium hydroxide; the kinetic runs were carried out in 8·3N-sodium hydroxide. The anomalous kinetic results can be interpreted in the light of previous work, where it has been shown that the isodiazo-species present in dilute and concentrated alkali are different and have different absorption spectra.

By using the values of $E_i$ and $E_n$ for 0·1N-sodium hydroxide, absorption spectra can be computed for different mixtures of normal and isodiazo-species in sodium hydroxide of this concentration. A calculated curve is shown broken in Fig. 2. The absorption maximum is at somewhat longer wavelength for the experimental curve, as is to be expected for an ionisation of the type $\text{isoArN}_2\text{·OH} \rightleftharpoons \text{isoArN}_2\text{O}^- + \text{H}^+$.

Since the true values for the extinction coefficient of the isodiazo-species in concentrated alkali cannot be measured accurately, an indirect method of calculation must be used to obtain a true rate constant for the normal to iso-transformation.

From equations (i) and (iv) one can write

$$(E_{\text{i}} - E_{\text{n}})/(E_{\text{i}} - E_{\text{n}}d_{\text{t}}/d_{\text{o}}) = a/(a - x),$$

and if $a/(a - x)$ is denoted by $A$ we obtain

$$E_{\text{i}} = \frac{E_{\text{n}}}{(A - 1)}\left(\frac{Ad_{\text{t}}}{d_{\text{o}}} - 1\right). \qquad \text{(v)}$$

If, from the experimental family of curves, a particular trace is selected as corresponding to a fixed amount of reaction (*i.e.*, a value of $A$ is assumed), an absorption curve can be calculated from equation (v) for the spectrophotometrically unknown isodiazo-species in concentrated alkali. For different selected values of $A$, different absorption curves result, and these, together with those calculated from other experimental traces form a family of curves for which each member is proportional to the true spectrum of the isodiazoate ion. While the true molar extinction coefficients do not result from these calculations the relative absorptions at different wavelengths and the position of the absorption maxima for the isodiazoate are obtained.

For a particular wavelength on a selected experimental curve, equation (v) can be written; at a second wavelength and for the same curve (*i.e.*, the same value of $A$) one can write:

$$E_{\text{i}} = \frac{E_{\text{n}}'}{(A - 1)}\left(\frac{Ad_{\text{t}}'}{d_{\text{o}}'} - 1\right). \qquad \text{(vi)}$$

If the two wavelengths are selected such that $E_{\text{i}} = E_{\text{i}}'$, then

$$(E_{\text{n}}Ad_{\text{t}}/d_{\text{o}}) - E_{\text{n}} = (E_{\text{n}}'Ad_{\text{t}}'/d_{\text{o}}') - E_{\text{n}}',$$

whence

$$A = \frac{E_{\text{n}} - E_{\text{n}}'}{(E_{\text{n}}d_{\text{t}}/d_{\text{o}}) - (E_{\text{n}}'d_{\text{t}}'/d_{\text{o}}')}. \qquad \text{(vii)}$$

Since $E_{\text{n}}$ and $E_{\text{n}}'$ are known, and $d_{\text{t}}$, $d_{\text{o}}$, $d_{\text{t}}'$, $d_{\text{o}}'$ are obtained experimentally, values of $A$ for each curve of the experimental family can be calculated. A plot of $\log_{10} A$ against $t$ should produce a straight line passing through the origin and having a slope equal to $k_1/2{\cdot}303$.

Thus a first-order rate constant for the isomerisation can be calculated by using the entire spectral range and at the same time eliminating uncertainty due to the unknown absorption spectrum of the isodiazoate.

## DISCUSSION

All the experimental results were considered as outlined above. Each kinetic run was treated independently, several empirical absorption curves corresponding to isodiazoate ion being calculated [equation (v)]. From these, at least four pairs of wavelengths having equal molar extinction coefficients were selected and used to calculate an $A$ value for each of the points in a run. The $A$ values plotted were thus the mean of at least four calculated values; in general, internal agreement was about ±2—5%. The experimental error is undoubtedly greater than this, since there are involved accumulated errors in $E_{\text{n}}$, uncertainty associated with tracing of the calculated curve for the isodiazoate ion, and concomitant difficulties in selection of wavelengths with equal extinction coefficients, particularly on steeper parts of the curve. A typical first-order plot calculated on this basis is shown in Fig. 3. The calculated first-order rate constants are listed in the Table. Also shown are the extreme rate constants as originally calculated by using the $E_{\text{i}}$ values for 0·1N-sodium hydroxide.

For the single run at 58·4°, a first-order rate constant, independent of the wavelength of measurement, could not be calculated. The calculated absorption spectrum of the reaction product [equation (v)] was not a simple curve with a single absorption maximum. Nor was the general form of the spectrum independent of the time of measurement. A spectrum calculated from an assumed $A$ value for a trace at the commencement of the run showed absorption maxima at about 275 and 300 mμ, the former being the more intense. Calculations for curves obtained later in the run produced spectra in which the band at 300 mμ showed stronger absorption. An interpretation of this different behaviour at the higher temperature is not obvious, since the phenoxide (the most likely decomposition product) does not show an absorption maximum in this region. It is clear, however, that the reaction followed is not a simple thermal isomerisation of the normal diazoate. This abnormal behaviour is not apparent in the experimental curves and emerges only in the calculated spectrum of the reaction product.

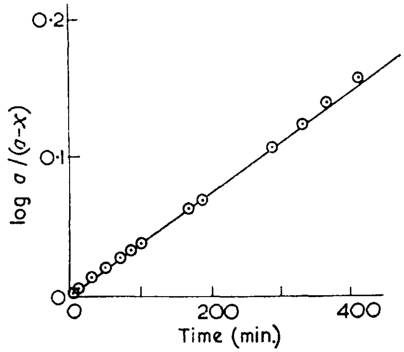

Fig. 3. First-order plot for thermal isomerisation of normal potassium *p*-sulphobenzenediazoate in 0·1N-NaOH.

First-order rate constants for the thermal isomerisation of the normal diazoate of sulphanilic acid.

| Temp. | 29·7° | 49·7° | 58·4° |
|---|---|---|---|
| $10^5k_1$ (sec.$^{-1}$), eqn. (iv), 268 mμ | 0·97 | 13·7, 13·3 | 44·8 |
| ,, ,, 300 mμ | 1·42 | 20·5, 18·3 | 66·3 |
| ,, eqn. (vii) | 2·0, 2·0 | 10, 12 | — |

*Conclusions.*—The rate constant measured at 49·7° is in agreement with the previous data of Le Fèvre and Sousa, while that at 29·7° is somewhat greater. The importance of the results lies in the fact that it is necessary to assume the isodiazo-species to be different in dilute and concentrated alkali if one is to obtain a rate constant which is independent of the wavelength of measurement. Strong support is thereby given to the previous contention [5] that the isodiazoate from sulphanilic acid is extensively hydrolysed in dilute alkali to the isodiazohydroxide.

University of Sydney, N.S.W., Australia.

[*Received, July* 30*th*, 1962