

The Determination of Arrhenius Parameters for a Normal-to-iso-diazoate Transformation.

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The change of the normal sodium diazoate from sulphanilic acid into its *iso*-isomer in aqueous sodium hydroxide is examined kinetically. The results indicate a frequency factor of 10^{13} — 10^{14} sec.⁻¹ and an energy of activation of 25—27 kcal./mole. This diazoate conversion thus resembles many others, studied previously with molecules containing $-N=N-$ and $-N^+NO^-$ groups where configurational inversions of *cis*- to *trans*-forms have been involved.

So far, the possibilities of geometrical isomerism with molecules generalisable as $X \cdot N : N \cdot Y$ have been considered by Le Fèvre and his collaborators for the cases (a) where X = an aryl or substituted aryl group and Y is one of the following radicals: Ph (*J.*, 1939, 531; 1948, 1949; 1949, 1595; 1952, 4082; 1953, 867), $-CN$ (*J.*, 1938, 431, 1878; 1947, 445, 457; 1949, 333, 944, 1106; 1950, 185, 3128), $-SO_2 \cdot O \cdot Metal$ (*J.*, 1951, 415), $-SO_2 \cdot Aryl$ (*J.*, 1952, 3381), $-CO \cdot NH_2$ (*J.*, 1951, 1977), $-NHAr$ (*J.*, 1951, 2743; 1952, 2932), or (b) where $X = Y = p-HO \cdot C_6H_4-$ (*J.*, 1939, 535), or (c) where $X = Y = C_5H_4N-$ (*J.*, 1951, 1814; compare Campbell, Henderson, and Taylor, *J.*, 1953, 1281). Observations relevant to examples contained in (a)—(c) are also given in *Chem. and Ind.*, 1948, 158, 543, 732, 782; 1953, 378; and in *Austral. J. Chem.*, 1953, 6, 341. Conclusions, in general, have been reconcilable with Hantzsch's stereochemical concept (*Ber.*, 1894, 27, 1702) that the $-N=N-$ unit can exist in a *cis*- or *trans*-configuration.

The objective of the present work was to supplement the above by a kinetic study of

the transformation of a normal to an *isodiazoate*, in which X = aryl or substituted aryl and Y (following Hantzsch's proposal) may be -O·Metal. At first sight the conditions necessary to bring about this change appear against the simple idea that it is geometric, for whereas diazocyanides, diazosulphonates, azobenzene, and various other azo-derivatives undergo interconversion spontaneously in non-polar solvents at low temperatures, the *n*-diazoates are often subjected to very concentrated alkalis at 100° or more during the preparations of their *iso*-forms. Less drastic treatment sometimes increases unwanted side-reactions. Jolles and Camiglieri (*Gazzetta*, 1932, **62**, 720) have reported that at 25° in 0·4N-aqueous sodium hydroxide the percentage conversions for the diazoates from aniline, *m*-toluidine, and *o*-anisidine are only 12—15, while from *p*-toluidine, *p*-phenetidine, and *p*-anisidine the yields are "traces," the rest being tar; Oddo, Indovina, Albanese, and Amatore (*ibid.*, 1935, **65**, 939), by examining 24 diazoates, including those from the *o*-, *m*-, and *p*-halogenoanilines, -nitroanilines, and -anisidines, have concluded that, in general, increased alkalinity decreases decomposition and raises the amount of *isodiazoate* obtained. The last group of authors utilised 0·4, 0·8, and 1·6% solutions of sodium hydroxide and estimated the nitrogen evolution, resin production, and quantity of *isodiazoate* formed in each case. The maximum yields of *isodiazoates* were of the order 75%, and always accompanied by considerable decomposition.

Our preliminary experiments confirmed the extensive decomposition suffered by most normal diazoates when treated with aqueous alkalis of a convenient concentration, *i.e.*, one at which the reaction mixture remained homogeneous during the change. We noticed, however, that Brown, Duffin, Maynard, and Ridd (*J.*, 1953, 3936), while tabulating quantitative data concerning the coupling of diazotised sulphanilic acid with glyoxaline, indicate that decomposition of the diazonium compound increases with pH until pH 10, after which one observation at pH 11 suggests that it decreases. (The "decomposition," whose first-order coefficients were around 10^{-5} sec.⁻¹, was estimated by coupling; this does not differentiate between actual decomposition and change into *isodiazoate*.) We confirmed this and ascertained that the sodium diazoate from sulphanilic acid undergoes 97—100% conversion into the *isodiazoate* in sodium hydroxide solutions ranging from 0·5 to 4·85N. It thus fulfilled our requirements.

EXPERIMENTAL

Sulphanilic acid was diazotised to give the solid diazobenzene-*p*-sulphonic acid. This was stirred with an equal weight of crushed ice, and 50% aqueous sodium hydroxide added gradually until a clear lemon-yellow solution was obtained. The latter, on cooling and treatment with more alkali, deposited crystals of the normal diazoate. A quantitative yield was obtainable by precipitation below 0° with 95% alcohol. The crystals were filtered by suction in air free from carbon dioxide, washed with cold alcohol, and dried *in vacuo*.

Solutions for the kinetic observations were made up in the range 0·0015—0·0036M with respect to the normal diazoate. A weighed quantity of the last-named was added to the sodium hydroxide solution (of appropriate concentration) which had been previously in a thermostat for some time. A further period was allowed for attainment of thermal equilibrium before measurements were begun. Samples (1 ml.) were then extracted and coupled with a slightly alkaline solution of β -naphthol. The Beer-Lambert law was found to hold under these conditions, colour being estimated by a Hilger Spekker photoelectric absorptiometer, a blue filter (Ilford 602) being used. The velocity constant was obtained from the slope of the graph $\log (E_0 - E_\infty)/(E_t - E_\infty)$ against time, where E_0 and E_∞ are the readings at the beginning and end of the experiments. Least-square methods gave essentially the same values of the velocity constant. The slopes of the straight lines so obtained for various concentrations of diazoate yielded constant values of k , indicating the applicability of first-order kinetics. This is the case for the total rate of change. It was established, by acidifying and coupling samples at the beginning and at the close of the experiments, that conversion was nearly quantitative (97—100%) for all strengths of alkali given in the Table. The values of k were therefore assumed to be those for the change of normal to *iso*-diazoate in the various media.

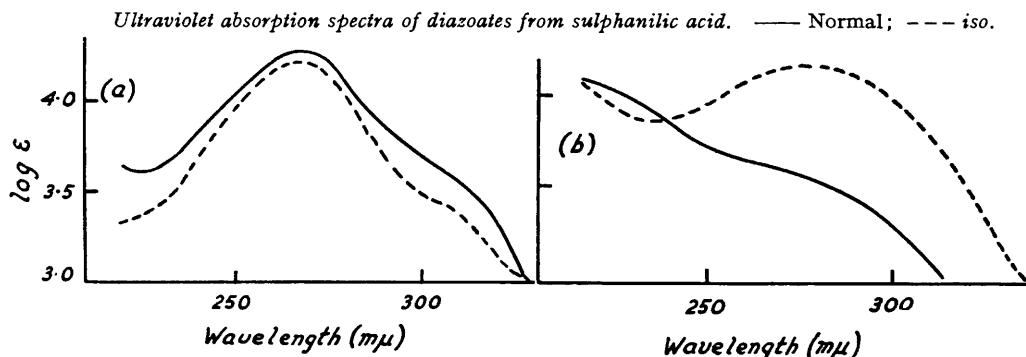
Results are set out in Table 1 which also includes the derived A and E terms of the Arrhenius equation.

TABLE I. Conversion of normal into iso-NaO·SO₂·C₆H₄·N₂·ONa.

Temp.	10 ⁴ k (sec. ⁻¹)	E (kcal./mole)	10 ⁻¹³ A (sec. ⁻¹)	Temp.	10 ⁴ k (sec. ⁻¹)	E (kcal./mole)	10 ⁻¹³ A (sec. ⁻¹)
	NaOH; 0.501N				NaOH; 2.2N		
40°	0.32	26.1	7.9	40°	0.2715	26.4	8.4 _s
50	1.57			50	1.395		
60	4.87			60	4.483		
65	8.10			65	7.082		
	NaOH; 1.292N				NaOH; 4.85N		
40	0.329, 0.320	25.4	2.1	40	1.1462	25.0	2.0
50	1.330, 1.300			50	1.469		
60	3.63, 3.59			60	6.32		
64.5	6.774			65	10.33		
	NaOH; 1.3N						
40	0.2967	25.7	4.1				
50	1.279						
60	3.761						
65	7.56						

DISCUSSION

The frequency factors and energies of activation (*viz.*, 10¹³–10¹⁴, and 25–27 kcal./mole) now ascertained for a normal→*iso*-diazotate change are similar to those previously reported for various inversions about the azo- and azoxy-groupings (see Table 2 for summary and references). They resemble also the values recorded for the transform-



ation of *cis*- into *trans*-piperonaldoximes (namely, 10¹³–10¹⁵, and 22–27 kcal./mole; Le Fèvre and Northcott, *J.*, 1949, 2235) but differ somewhat from the figures found for the interconversion of the stilbenes (10¹⁰, and 36.7 kcal./mole; Taylor and Murray, *J.*, 1939, 2078). There is nothing here against the existence of a common mechanism for all cases where the double bond involves at least one nitrogen atom. A point of interest now revealed is the smallness of the effect on the kinetics of varying the medium from aqueous alkali through polar to non-polar liquids or the solute from the electrovalent diazoates to the covalent azo- and azoxy-benzenes. By analogy therefore our belief is strengthened that the isomerisation of normal diazoates is geometrical in nature and essentially concerns the anions.

Absorption Spectra of the Isomeric Sodium Diazoates from Sulphanilic Acid.—In aqueous solutions both forms absorb strongly and similarly at 270 mμ (log ε 4.2); the log ε–wavelength plots indicate that the absorptions are more intense below 200 mμ. Minima occur at 225 mμ. Rather broad shoulders are found between *ca.* 290 (log ε 3.8) and *ca.* 320 mμ (log ε 3.2). The spectra (Fig. a) are otherwise featureless, and in general shape reminiscent of that for *N*-methyl-*N*-nitrosoaniline in alcohol (λ_{max} 275 mμ, log ε 3.9; Earl, Le Fèvre, and Wilson, *J.*, 1949, S 103). These results differ somewhat where relative intensities are concerned from those secured in dilute aqueous sodium hydroxide by Hantzsch and Lifschitz (*Ber.*, 1912, 45, 3029) whose graph indicated that at *ca.* 286 mμ the “*anti*” salt exhibited a maximum absorption while the “*syn*” salt absorbed less strongly and displayed

a very broad inflexion. Repetition, however, in 0.1N-sodium hydroxide solution (Fig. *b*) confirms Hantzsch and Lifschitz's findings.

We mention specifically that the coupling powers of our solutions were checked by experiment, and that the contrast in this ability was retained after the determinations of absorption were completed.

TABLE 2. *Summary of previous kinetic studies involving geometrical change about the -N=N- group.*

<i>cis</i> -to- <i>trans</i> -Change	Solvent	<i>A</i>	<i>E</i> (kcal./mole)	Reference
<i>p</i> -Br·C ₆ H ₄ ·N:N·CN	C ₆ H ₆	ca. 10 ¹³	ca. 22	Le Fèvre and Vine, <i>J.</i> , 1938, 431
α - and β -C ₁₀ H ₇ ·N:N·CN	C ₆ H ₆	10 ¹³	23	Le Fèvre and Northcott, <i>J.</i> , 1949, 333
<i>p</i> -Cl·C ₆ H ₄ ·N:N·CN	8 various	10 ¹¹ —10 ¹⁵	21—26	<i>Idem, ibid.</i> , p. 944
<i>p</i> -X·C ₆ H ₄ ·N:N·CN (X = H, Me, Cl, Br, NO ₂ , and MeO) and 2 : 4 : 6- Br ₃ C ₆ H ₃ ·N:N·CN	C ₆ H ₆	10 ¹¹ —10 ¹⁵	21—26	" "
C ₆ H ₅ ·C ₆ H ₄ ·N:N·CN	C ₆ H ₆	10 ¹¹	22	Freeman and Le Fèvre, <i>J.</i> , 1950, 3128
4'-Br·C ₆ H ₄ ·C ₆ H ₄ ·N:N·CN C ₆ H ₅ ·N:N·C ₆ H ₅	C ₆ H ₆ 16 various	10 ¹³ 10 ¹² —10 ¹⁴	21.5 22—25	Halpern, "Brady, and" Winkler, <i>Canad. J. Res.</i> , 1950, 28, D. 140
C ₆ H ₅ ·N:N(O)·C ₆ H ₅	9 various	10 ¹² —10 ¹⁵	22—25	Luner and Winkler, <i>Canad. J. Chem.</i> , 1952, 30, 679
4 : 4'-Me·C ₆ H ₄ ·N:N(O)·C ₆ H ₄ Me C ₆ H ₅ ·N:N·C ₆ H ₅	" 7 various	10 ¹³ —10 ¹⁶ 10 ¹⁰ —10 ¹³	22—24 22—28	Le Fèvre and "Northcott, <i>J.</i> , 1953, 867
<i>p</i> -X·C ₆ H ₄ ·N:N·C ₆ H ₅ (X = Me, Cl, Br, NO ₂ , and MeO)	C ₆ H ₆	10 ¹⁰ —10 ¹²	22—25	" " "

Nujol mulls of the solid isomers used in the above kinetic study give infrared spectra having dissimilarities. Table 3 lists the bands recorded together with—for comparison—those from sodium sulphanilate.

TABLE 3. *Infrared absorptions.*

Normal diazoate	<i>iso</i> -Diazoate	Na sulphanilate	Assignment	Normal diazoate	<i>iso</i> -Diazoate	Na sulphanilate	Assignment
3630 (w)		—	Combined H ₂ O	1195 (s, broad)	1195 (s, broad)	1173 (ms)	C-H rocking
1923	1918 (w)	3463 (s)	N-H	1132 (m)	1132 (m)	1120 (ms)	C-N
1622	1692 (w)	1654 (m)	Combined H ₂ O	1107 (w)	1107 (m)	1033 (ms)	See text
	1599	1625 (m)		1034	1045	1000 (ms)	ν_{14} of benzene
	1580 (w)	1599 (m)		1009	1010 (w)	1000 (ms)	(SO ₂ ·O) ⁻
		1503 (w)		917	917	947 (w)	See text
	1417 (w)	1457 (w)		842	845	835 (s)	<i>p</i> -Disubstd. benzene
		1436 (w)		823 (w)			
1307 (w)	1302 (w)	1376 (m)	C-N	786			
1284 (w)		1302 (ms)		750	756	721	Ar ring
		1282 (ms)	(SO ₂ ·O) ⁻ ?			697 (s)	
		1237 (ms)					

It is seen that only two absorptions are common to the isomeric diazoates and absent from sodium sulphanilate, *viz.*, those at 1107 and 917 cm.⁻¹. When this is considered in conjunction with the bands found for other diazo-derivatives (Le Fèvre, O'Dwyer, and Werner, *Austral. J. Chem.*, 1953, 6, 341) the 1107-cm.⁻¹ band did not appear with the labile potassium benzene diazoate. It is unlikely therefore to be the N-O⁻ frequency which we were hoping to reveal. The feature at 917 cm.⁻¹ likewise cannot be due to N-O⁻ since all azo-compounds, including diazoates, examined to date, absorb near this point (*cis*- and *trans*-azobenzenes, 918 and 923 cm.⁻¹; diazosulphonates, *ca.* 960 cm.⁻¹; diazosulphonates, 880—944 cm.⁻¹; azopyridine, 960 cm.⁻¹; azomethane, 932 cm.⁻¹; 1-methyl-1 : 2 : 3-benzotriazole, 936 cm.⁻¹; cf. Le Fèvre, O'Dwyer, and Werner, *loc. cit.*).

Tetlow (*Research*, 1950, **3**, 187) ascribes the band (recorded by him at 927 cm.^{-1}) in the azobenzenes to the fragment $\text{C}=\text{N}=\text{N}-\text{C}$, but its emergence in diazoates and the triazole must limit this suggestion to $\text{C}=\text{N}=\text{N}-\text{X}$, where X is not a carbon atom.

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