

### 479. *Effects of Solvents on the Thermal Interconversion of the Piperonaldoximes.*

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The rates of isomerisation of piperonaldoxime, m. p. 144°, to that of m. p. 112°, have been studied dilatometrically in seven media, each at two temperatures. Energies of activation and frequency factors are calculated and discussed in relation to solvent properties. An empirical expression,  $E_{\text{observed}} = 24.5 + 2.7 \log_{10} \mu_{\text{solvent}}$ , is found to correlate the results satisfactorily. Comparisons are made with analogous data for systems containing  $\text{-C=C-}$  and  $\text{-N=N-}$ . The dipole moments of the two oximes are found to be 1.5<sub>5</sub> and 1.7<sub>5</sub> D., respectively.

In a previous paper (this vol., p. 944) on the kinetics of geometrical change of the  $\text{-N=N-}$  group we noted the paucity of data for related  $\text{C=C-}$  or  $\text{C=N-}$  containing systems in the dissolved condition. Certain oxime-inversion studies by Patterson and collaborators (*J.*, 1907, **91**, 504; 1908, **93**, 1941; 1912, **101**, 26, 2100; 1941, 606) were on record, it is true, but these had the disadvantage that, being obtained polarimetrically, they involved media which were always mixtures rich in ethyl tartrate. Our observations, for which we desired to find comparisons, had been made in *single* solvents. Moreover, only in the case of piperonaldoxime had Patterson *et al.* (*loc. cit.*, 1908) determined reaction constants at different temperatures, but from these we had found that *A* and *E* (in the usual Arrhenius equation) could not be evaluated with satisfactory certainty. We accordingly decided to reinvestigate the last change in several of the liquids used by us for the diazocyanides (Le Fèvre and Northcott, *loc. cit.*).

*Dipole Moments of the Isomeric Piperonaldoximes.*—The measurements recorded in Table I were made to ascertain whether changes in dielectric constant would be adequate for following the spontaneous (thermal) isomerisation of the oxime of m. p. 144° to that of m. p. 112°. The solutes were prepared by the methods indicated by Patterson and McMillan (*loc. cit.*, 1908).

Experimental procedures and symbols, etc., are as defined in earlier papers (*e.g.*, *J.*, 1937, 1805; this vol., p. 333), the solvent being benzene, and the temperature 25°.

TABLE I.

$10^6 \times w_1$ 0	$\epsilon_{1000}^{25}$ Kc. 2.2725	$d_1^{25}$ 0.87378	$\alpha\epsilon_2$ —	$\beta d_2$ —
Labile oxime, m. p. 144°.				
802.0	2.2738	0.87402	1.64	0.301
1,789.0	2.2755	0.87436	1.67 <sub>5</sub>	0.323
2,057.9	2.2760	0.87433	1.70	0.269
2,582.0	2.2767	0.87458 <sub>5</sub>	1.63	0.312
3,044.3	2.2776	0.87470	1.67 <sub>5</sub>	0.301
Stable oxime, m. p. 112°.				
2,388.3	2.2769	0.87433	1.90	0.237
3,182.7	2.2791	0.87454	2.07	0.240
5,530.0	2.2833	0.87504	1.96	0.228
9,169.7	2.2908	0.87594	1.99 <sub>5</sub>	0.240
13,376.0	2.2982	0.87703	1.92	0.243

Since the  $\alpha$  and  $\beta$  factors display no signs of smooth concentration dependence (contrast Calderbank and Le Fèvre, this vol., p. 1462) polarisations are computed from the arithmetic means:

Oxime.	$M_1$ .	Mean $\alpha E_2$ .	Mean $\beta$ .	$\infty P_1$ .	$[R_L]_D$ .	$\mu$ D.
m. p. 144°	165.15	1.66	0.345	88.4	39	1.5 <sub>5</sub>
m. p. 112°	„	1.99	0.272	102.2	„	1.7 <sub>5</sub>

With the benzaldoximes (Calderbank and Le Fèvre, *loc. cit.*) the more stable oxime has the lower m. p. and dipole moment. In the last-named respect, the piperonaldoximes are related in the opposite way. This is not in itself significant since (cf. this vol., p. 2374) the effect of the methylenedioxy-chain is to produce an additional vector acting with its negative pole towards the aromatic nucleus.

*Isomerisation Rates of the Labile Piperonaldoxime.*—With the data of Table I as a guide, it was obvious that density, rather than dielectric constant, would be the better rate-indicating property

for the present purpose. Since the actual evaluation of this as a function of time has no intrinsic relevance, *volume* changes have been observed instead. Dilatometers resembling those styled "Type C" in Fig. 1 of *J.*, 1938, 932 (Benford and Ingold), but of uniform bore throughout, were constructed from Pyrex capillary tube. They, with stoppered flasks holding predetermined quantities of the seven pure liquids of Table II, were immersed in thermostats set at 25° or 42.5°, the solute (weighed by difference) added to the solvent (this operation being taken as occurring at zero time in subsequent calculations), and the solution so formed sucked into the dilatometer *via* the inverted side arm. A scale (from a Beckmann thermometer) attached above the bulb allowed the expansion to be easily read with sufficient accuracy. The solvents were as specified in our previous paper (this vol., p. 944). Table II shows the first-order reaction constants found at each of the two temperatures together with frequency factors and energies of activation calculated therefrom.

FIG. 1.

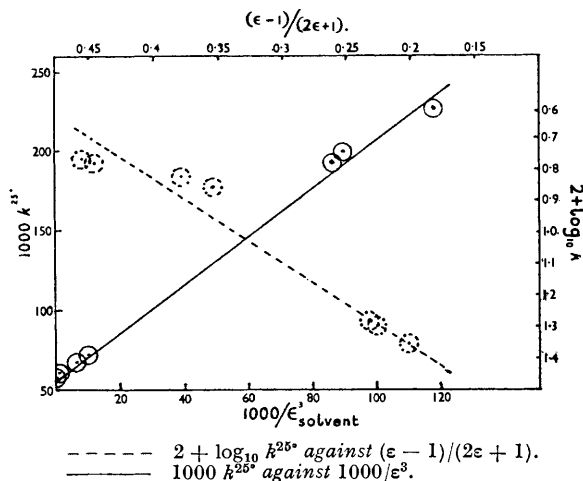


TABLE II.

Solvent.	$k^{25}$ (hrs. <sup>-1</sup> ).	$k^{42.5}$ (hrs. <sup>-1</sup> ).	$E$ (kcal./g.-mol.).	$A$ (secs. <sup>-1</sup> ).
<i>cyclo</i> Hexanone .....	0.059	0.71 <sub>7</sub>	26.6	$5.9 \times 10^{15}$
Pyridine .....	0.061	0.72 <sub>3</sub>	26.3	$3.8 \times 10^{15}$
Chlorobenzene.....	0.068	0.78	25.9 <sub>5</sub>	$2.3 \times 10^{15}$
Chloroform .....	0.072	0.80 <sub>6</sub>	25.7	$1.4 \times 10^{15}$
Benzene .....	0.193 <sub>5</sub>	1.62	22.6	$2.5 \times 10^{13}$
Carbon tetrachloride .....	0.200	1.7	22.8	$3.4 \times 10^{13}$
<i>cyclo</i> Hexane .....	0.227	—	—	—

*Discussion.*—It is of interest first to compare our results with those of Patterson and McMillan (*loc. cit.*, 1908). These authors recorded first-order reaction constants between 20° and 30° in 2° steps, using ethyl tartrate as a solvent. Application of the Arrhenius equation to the various possible pairs of  $k_t$  gives, we find, a range of  $E$  values from 18 to 29 kcal./g.-mol. (the majority lying between 22 and 27 kcal./g.-mol.) and a related series for  $A$  from  $10^{14}$  to  $10^{17}$  sec.<sup>-1</sup>. These figures are seen to be of an order comparable with those in Table II.

We will now compare the data of Table II with our observations (this vol., p. 944) on the *cis*- → *trans*-*p*-chlorobenzene diazocyanide inversions in the same media. Although the solvents do not affect both reactions in an identical manner the same general tendencies are seen.

Thus the velocities at 25° are :

for *p*-Cl·C<sub>6</sub>H<sub>4</sub>·N<sub>2</sub>·CN : *cyclo*hexanone < C<sub>5</sub>H<sub>5</sub>N < C<sub>6</sub>H<sub>6</sub> < CCl<sub>4</sub> < CHCl<sub>3</sub> < C<sub>6</sub>H<sub>5</sub>Cl < C<sub>6</sub>H<sub>12</sub>

for CH<sub>2</sub>O<sub>2</sub>·C<sub>6</sub>H<sub>5</sub>·CH·NOH : *cyclo*hexanone < C<sub>5</sub>H<sub>5</sub>N < C<sub>6</sub>H<sub>5</sub>Cl < CHCl<sub>3</sub> < C<sub>6</sub>H<sub>6</sub> < CCl<sub>4</sub> < C<sub>6</sub>H<sub>12</sub>

The only significant difference is the position of chlorobenzene, since for the diazocyanide the magnitudes of  $k_{25}$  in benzene, carbon tetrachloride, and chloroform were similar.

The reaction is faster the lower the dielectric constant or the dipole moment appropriate to each solvent. Most of the correlations attempted previously (Le Fèvre and Northcott, *loc. cit.*)

for the diazo-compounds are slightly more satisfactory with this oxime, *e.g.*, plots of  $k$  against  $\epsilon$ ,  $1/\epsilon$ , or  $1/\epsilon^2$ , can be drawn to appear as imperfect curves; the plot of  $k$  against  $1/\epsilon^2$  shows more rectilinearity (see Fig. 1).  $\log k$  likewise varies with the dielectric constant of the solvent—its possible connection with  $(\epsilon - 1)/(2\epsilon + 1)$  is included, as one example, in Fig. 1 (cf. Glasstone, Laidler, and Eyring, "The Theory of Rate Processes," McGraw-Hill, 1941, p. 420). Similarly,

FIG. 2.

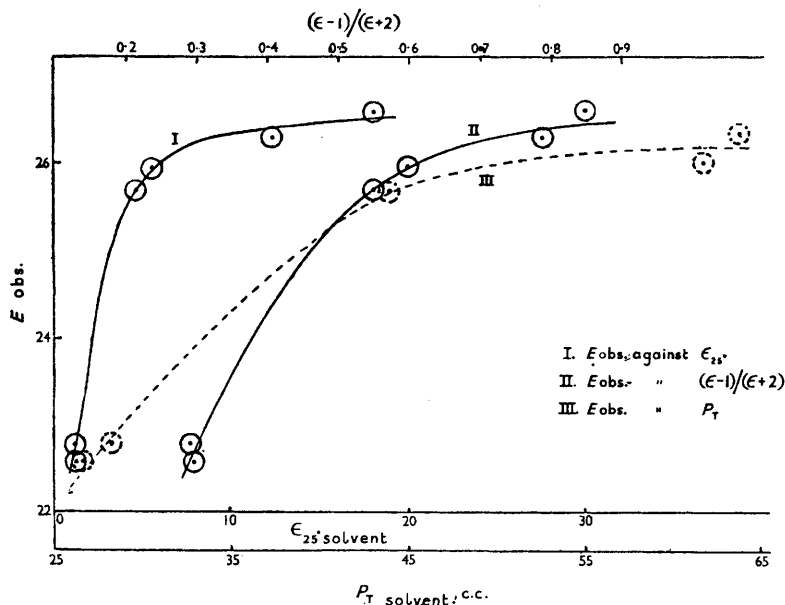
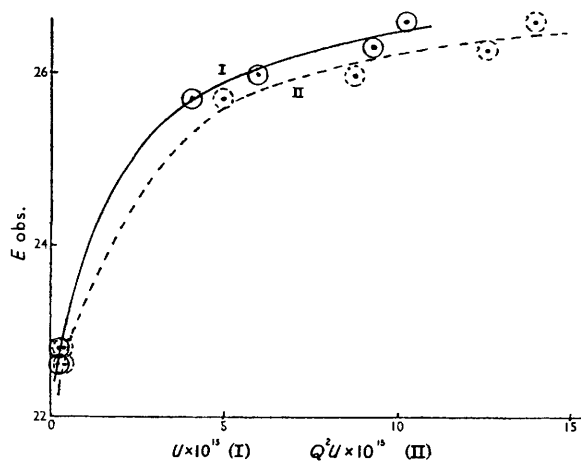


FIG. 3.



$E_{\text{obs.}}$  (from Table II) may be represented fairly smoothly against  $\epsilon_{\text{solvent}}$  or derivatives of it (see Fig. 2), or  $\mu_{\text{solvent}}$ , or  $U$  or  $Q^2 U$  (see Fig. 3).

The last two quantities represent an attempt to estimate relative electrostatic interaction energies for different solvent-solute combinations; details and definitions are as already published (this vol., p. 944). The necessary data for Figs. 1-3 are in Table III,  $\mu_{\text{solute}}$  being taken as 1.65 D. and  $r_{\text{solute}}$  as *ca.* 4.5 Å.

With *p*-chlorobenzene diazocyanide the plots of  $E_{\text{obs.}}$  against  $U$  (or  $Q^2 U$ ) approximated to

TABLE III.

	$\epsilon_{\text{solvent}}^{25}$	$\mu_{\text{solvent}}$ , D.	$\alpha \times 10^{23}$ , C.C.*	$r_{\text{solvent}}$ , A.†	$\mu_{\text{M}} \times 10^{18}$	$U \times 10^{15}$	$Q^2U \times 10^{15}$
<i>cyclo</i> Hexanone ...	18.2	2.8	1.09	3.12	2.8 <sub>8</sub>	10.5	14.0
Pyridine .....	12.4	2.3	0.95	2.87	2.3 <sub>8</sub>	9.3	12.6
Chlorobenzene ...	5.61	1.6	1.22	3.10	1.6 <sub>9</sub>	6.0	7.8
Chloroform .....	4.72	1.0	0.84	2.87	1.1 <sub>7</sub>	4.1	5.0
Benzene .....	2.27	0	1.03	2.96	0.08 <sub>3</sub>	0.3 <sub>3</sub>	0.3 <sub>3</sub>
Carbon tetra- chloride .....	2.23	0	1.04	3.05	0.080	0.3 <sub>1</sub>	0.3 <sub>3</sub>
<i>cyclo</i> Hexane .....	2.04	0	1.09	3.16	0.080	0.2 <sub>8</sub>	0.3 <sub>1</sub>

\*  $\alpha = 0.0394 [R_L]_D \times 10^{-23}$  c.c.†  $r_{\text{solvent}} = (0.2916 M/d)^{\frac{1}{2}} \times 10^{-8}$  cm.

straight lines, and there was no direct relation between  $E_{\text{obs.}}$  and  $\mu_{\text{solvent}}$ . For piperonaldoxime the connection seems to be hyperbolic, plots of  $E_{\text{obs.}}$  against  $\log \mu$  or  $\log Q^2U$  showing fair rectilinearity, suggesting that  $E_{\text{obs.}}$  may be written as  $(25.4 + 2.7 \log_{10} \mu)$  kcal./g.-mol., or, if  $\mu_{\text{M}}$  be used, as  $(25.4 + 2.45 \log_{10} \mu_{\text{M}})$ :

	<i>cyclo</i> Hexanone.	C <sub>5</sub> H <sub>5</sub> N.	C <sub>6</sub> H <sub>5</sub> Cl.	CHCl <sub>3</sub> .	C <sub>6</sub> H <sub>6</sub> .	CCl <sub>4</sub> .
$E_{\text{obs.}}$ .....	26.6	26.3	25.9 <sub>5</sub>	25.7	22.6	22.8
$E_{\text{calc.}}$ (using $\mu$ ) .....	26.6	26.4	25.9 <sub>5</sub>	25.4	22.7	22.7
$E_{\text{calc.}}$ (using $\mu_{\text{M}}$ ) .....	26.5	26.3	25.9 <sub>6</sub>	25.6	22.7	22.7

Since ethyl tartrate has  $\mu = 3.1$  D. at 25° (Faraday Soc. List, 1934), we would expect  $E_{\text{obs.}}$  to be 26.7<sub>3</sub> kcal./g.-mol in this solvent. Such a value is within the range of those calculable from Patterson and McMillan's data (see above).

*Mechanism of the Reaction.*—Intuitively the geometrical inversion of a  $>C=N^-$  grouping might be expected to be kinetically intermediate between analogous changes about  $>C=C<$  and  $-N=N^-$  linkages. The energies of activation now observed for piperonaldoxime resemble those obtained for *p*-chlorobenzenediazocyanide and, where  $E$  is concerned, show no effects of the replacement of nitrogen by carbon. It can, however, be urged that the instances just mentioned are improper comparisons, since the activating effects of the attached groups are ignored. Such a view may be justified by considering the series: Ph—N=N—Ph, Ph—CH=N—Ph and Ph—CH=CH—Ph. Here the first and the third member exist in isomeric forms which are interconvertible, whilst the second has so far been found only as the *trans*-structure (de Gaouck and Le Fèvre, *J.*, 1938, 741; 1939, 1392). Yet even among the oximes themselves a similar variability of stability occurs (*e.g.*, compare the piperonaldoximes with certain other aryl oximes known in single forms only; Brady and Dunn, *J.*, 1914, 105, 821, 2409; 1915, 107, 1858; 1916, 109, 667; Brady *et al.*, *J.*, 1920, 117, 1045; 1925, 127, 2427; 1927, 894). Since azo-compounds are isoelectronic with corresponding molecules containing  $>C=N^-$  and  $>C=C<$  there is no *a priori* reason why the potential energy–torsional rotation relations for analogous members of the three classes should not be fundamentally similar. For olefins, Magee, Shand, and Eyring (*J. Amer. Chem. Soc.*, 1941, 63, 667; cf. Glasstone, Laidler, and Eyring, *op. cit.*, p. 324) have discussed the possibility of two alternative reaction paths, one adiabatic with frequency factors of *ca.*  $10^{13}$  sec.<sup>-1</sup>, the other non-adiabatic for which this quantity is many powers of ten lower. In the former the singlet state persists throughout; in the latter there is, through electronic transition, intervention of the triplet state, which for ethylene may be considerably below the intersection of the potential energy–torsional rotation curves for the *cis*- and *trans*-configurations.

The frequency factors now reported for piperaldoxime ( $10^{13}$ – $10^{15}$  sec.<sup>-1</sup>) and those previously noted for various azo-derivatives ( $10^{12}$ – $10^{15}$  sec.<sup>-1</sup>; Le Fèvre and Northcott, *loc. cit.*) in no way suggest non-adiabatic mechanisms. It would seem therefore that these isomerisations are to be compared with those of stilbene and its halogenated derivatives in the liquid phase ( $A = 10^{10}$ – $10^{11}$  sec.<sup>-1</sup>;  $E = 34$ – $37$  kcal./g.-mol.) rather than other olefins ( $A = 10^4$ – $10^5$  sec.<sup>-1</sup>,  $E = 16$ – $27$  kcal./g.-mol.), which at first sight appear to have more parallel energy factors (cf. Le Fèvre and Northcott, *loc. cit.*, for references). Our reactions may be examples where resonance in the activated state so lowers the intersection point (cf. above) that paths *via* triplet states never have an advantage (Magee, Shand, and Eyring, *loc. cit.*). The different  $E$  values for  $-CH=CH-$  and  $-N=N^-$  systems could be understood if the resonance energies of members of the latter class were significantly greater than those of the former. Coates and Sutton (*J.*, 1948, 1187) have recently considered the energy excesses between the “normal” (*i.e.*, with central double bond) and possible activated (*i.e.*, with central single bond) structures of

stilbene, azobenzene, and benzylideneaniline. They argue (cf. formulæ, *loc. cit.*, p. 1192) that the order of resonance energies should be  $\text{Ph}-\text{N}=\text{N}-\text{Ph} > \text{Ph}-\text{CH}=\text{N}-\text{Ph} > \text{Ph}-\text{CH}=\text{CH}-\text{Ph}$ . Qualitatively therefore, that  $E_{\text{azobenzene}}$  is less than  $E_{\text{stilbene}}$  can be understood *a priori*, although why the intermediate anil has not yet been isolated in separate forms remains unclear.

On the same basis the action of polar solvents (on the oxime and various azo-derivatives) in slowing the inversion reaction *and* raising its energy of activation can be roughly ascribed to a diminution of resonance in the solute. Each solvent molecule, by direct electrostatic-field effects, will first cause induced moments in the polarisable solute and then tend to associate with it. A dissymmetrical electrical environment being thus produced, it is plausible that a *diminution* of electron mobility (reversible conjugation), and therefore of resonance energy, should result. This is equivalent to saying that the intersection point (see above) has moved away from the line representing the ground state.

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