Thermal Decomposition and Isomerisation of *cis*-Azoisopropane

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Summary Arrhenius parameters for the decomposition and isomerisation of *cis*-azoisopropane have been determined and correlated with spectral and thermochemical data.

The thermal decompositions of *trans*-azoalkanes have been widely studied[1,2] but little is known about the thermal reactions of the *cis*-isomers although the latter have been isolated.[3,4] Photochemical *cis–trans*-isomerisation has been observed[3] and although the corresponding thermal reaction has not been reported it has been pointed out[2] that the decomposition of the *trans*-form could in fact proceed *via* the more labile *cis*-form. We now show that thermal *cis–trans*-isomerisation does occur and with a lower activation energy than decomposition but, because of unfavorable *A*-factors, is less important than direct decomposition for both *cis*- and *trans*-isomers in the temperature ranges commonly employed. Also the kinetic, thermochemical, and spectral data can be unified and indicate that the transition state(s) for decomposition and the first excited state(s) are very similar for both isomers.

cis-Azoisopropane (I) was prepared from the *trans* isomer (II) by naphthalene-sensitized isomerisation.[5] The pyrolysis of (I) was carried out in iso-octane over the range 388—425 K. Besides N_2, the only products observed by v.p.c. were (II) [(I) → (II), k_1, isomerisation] and C_3 and C_6 hydrocarbons [(I) → $2C_3H_7\cdot + N_2$, k_2, decomposition] with the data fitting first-order kinetics. Analyses of samples which had been pyrolysed from 10 to 100% indicated that, to within ± 3%, $[(\mathrm{I})]_0 = [(\mathrm{I})]_t + [(\mathrm{II})]_t + [C_6]_t + \frac{1}{2}[C_3]_t$ so that no significant products were omitted. Since (I) has $\epsilon = 140\ \mathrm{l\ mol^{-1}}$ at its $n \rightarrow \pi^*$ maximum (380 nm) and of the products only (II) has a small absorbance at this wavelength ($\epsilon = 9{\cdot}1\ \mathrm{l\ mol^{-1}\ cm^{-1}}$) it was generally most convenient to follow the reaction spectrophotometrically, opening the sample finally for confirmatory v.p.c. analysis. Both methods gave good agreement. A non-polar solvent was employed so that gas- and solution-phase data could be directly compared. The decomposition of azo-t-butane (ATB) has almost identical rates in both phases.[6] Also spectral data in both phases are very similar.[3,5] However, solution-phase studies are more convenient in that besides avoiding surface effects[7] they minimize radical reactions with the azo-compound.[2]

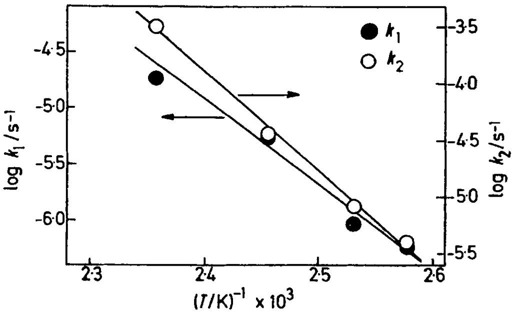

FIGURE. Arrhenius plots for the isomerisation (k_1) and decomposition (k_2) of *cis*-azoisopropane in iso-octane.

The Arrhenius plots in the Figure yield $\log k_1/\mathrm{s}^{-1} = (12{\cdot}4 \pm 1{\cdot}6) - (138 \pm 12\ \mathrm{kJ\ mol^{-1}})/2{\cdot}303\ RT$ and $\log k_2/\mathrm{s}^{-1} = (17{\cdot}5 \pm 0{\cdot}9) - (170 \pm 7\ \mathrm{kJ\ mol^{-1}})/2{\cdot}303\ RT$. Thus despite the fact that the activation energies are such that $E_2 > E_1$, because of the high value of the A-factor A_2, $k_2 > k_1$ over the temperature range used. Such high A-factors for azoalkane decompositions are common.[1,8] It has been estimated that $\Delta H_f(\mathrm{I}) - \Delta H_f(\mathrm{II}) = ca.$ 37 kJ mol^{-1} [9,10] so that for (II) → (I), k_{-1}, $\log k_{-1}/\mathrm{s}^{-1} = ca.$ $12{\cdot}4 - (175\ \mathrm{kJ\ mol^{-1}})/2{\cdot}303\ RT$. In the most recent study[11] of the decomposition of (II) [(II) → $2\mathrm{C_3H_7}\cdot + \mathrm{N_2}$, k_3, $\log k_3/\mathrm{s}^{-1} = 16{\cdot}6 - (200\ \mathrm{kJ\ mol^{-1}})/2{\cdot}303\ RT$, so that at 800 K, the median temperature used, $k_3 = 400\ k_{-1}$. This means that pyrolysis of (II) does not proceed *via* the labile *cis*-isomer.

The similarity in the difference between the decomposition activation energies $(E_3 - E_2) = 30 \pm 11\ \mathrm{kJ\ mol^{-1}}$ and $\Delta H_f(\mathrm{I}) - \Delta H_f(\mathrm{II})$ means that both transition states have similar enthalpies and therefore possibly related structures. The above activation energy difference may also be compared with the corresponding 83 kJ mol^{-1} difference for *cis*- and *trans*-ATB.[12] This reflects the much larger steric strain for *cis*-ATB and implies a greater difference between their heats of formation. These differences are mirrored in the positions of the $n \rightarrow \pi^*$ maxima. For ATB in methanol[12] the *cis*-isomer absorption is red-shifted by 59 kJ mol^{-1}, while the absorption for (I) is red-shifted by *ca.* 19 kJ mol^{-1} from that for (II) in both iso-octane and water. This would be expected if the first excited state of both isomers were essentially common.[3]

Calculations indicate that the isomerisation of aromatic azo-compounds should proceed by inversion rather than rotation.[13] The experimental value for the isomerisation activation energy of azobenzene is 94 kJ mol^{-1} but there would appear to be significant interaction between the π-electrons of the aromatic ring and the n-electrons of the rehybridizing nitrogen. The corresponding calculations have not been carried out for azoalkanes but for methylenamine, $\mathrm{CH_2{=}N{-}H}$, the inversion barrier has been estimated to be 113 kJ mol^{-1} [14] while the experimental isomerisation energy for difluorodiazine is 135 kJ mol^{-1}.[15] These data together with our value of 138 kJ mol^{-1} for the activation energy of (I) → (II) suggest this is also a case of inversion, but accurate quantum mechanical calculations would be welcome.

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