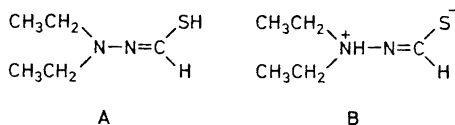


Derivatives of Hydrazine

VI. The Structure of Thioformyl
N,N-DiethylhydrazineU. ANTHONI, P. JAKOBSEN, Ch. LARSEN
and P. H. NIELSEN*Chemical Laboratory II (General and Organic Chemistry), University of Copenhagen, The H. C. Ørsted Institute, Copenhagen, Denmark*

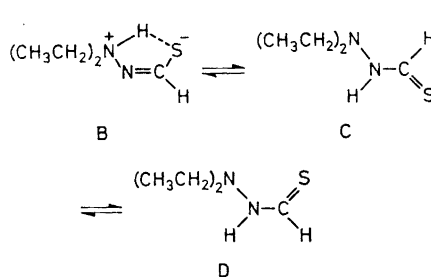
In a recent communication¹ Bredereck *et al.* pointed out that the infrared spectrum of thioformyl-*N,N*-diethylhydrazine (I) recorded in a KBr pellet contrasted to the infrared spectra of thioformyl-*N,N*-diisopropylhydrazine and *N*-thioformyl-amino-2,6-dimethylpiperidine by lacking both the NH stretching absorption around 3130 cm⁻¹ and the band characteristic of thioureides around 1550 cm⁻¹.² Instead a strong band at 2776 cm⁻¹ had appeared in the spectrum of (I), which was assigned to the SH stretching vibration of the iminothioform (A).



Bellamy³ quotes limits of 2550–2600 cm⁻¹ for the SH stretching absorption remarking that, exceptionally, it can be found at lower wavenumbers (2350 cm⁻¹ in 1,2-ethanedithiol) but probably not at higher wavenumbers than 2688 cm⁻¹, which is the value reported for hydrogen sulfide. In order to clarify whether the above assignment is correct, (I) was prepared by the method described by Bredereck *et al.* and its identity confirmed by elemental analysis and m.p.. In that part of the infrared region extending from 2500–2800 cm⁻¹ the spectrum of (I), recorded in a KBr pellet, displayed three well-defined absorptions with maxima at 2775 cm⁻¹ (strongest), 2737 cm⁻¹, and 2680 cm⁻¹ (weakest). By repeated recrystallization of (I) from CH₃OD the mobile hydrogen atom was exchanged with deuterium. The infrared spectrum of the deuterated compound showed that the three absorptions had been displaced to 2149 cm⁻¹ (strongest), 2116+2100 cm⁻¹,

and 2073 cm⁻¹ (weakest). Since these results establish that the absorption originates from, respectively, hydrogen and deuterium stretching vibrations, it was assigned to an N⁺-H group rather than to an S-H group since the infrared absorption of the latter always appears as a single band.³ The structure of (I) in the solid state was therefore concluded to be (B) and not (A). In support of this, the only other significant change in the infrared spectrum of (I) on deuteration was the displacement of a very strong absorption at 1270 cm⁻¹ to 979 cm⁻¹. This cannot be explained if the structure of (I) is (A) but the bands do, however, lie in the region where N⁺-H deformations are expected to occur.⁴

Absorptions in the NH-stretching region in the IR spectra of (I) and the deuterated compound in CHCl₃ showed that small amounts of the nonpolar thioformyl form were present in addition to the dipolar form B. By investigation of the PMR spectrum of (I) in CDCl₃ it was possible to obtain definite proof that the two species in equilibrium were the dipolar form B and the nonpolar form C in which the CH and the NH protons are *trans* to each other.



From the PMR spectra of (I), recorded in CD₃OD and CDCl₃ solution, it was deduced that the percentage amounts of the polar and the nonpolar form were dependent not only on the solvent used, but were also changed on storage. A freshly prepared solution of (I) in CDCl₃ at 40°C contained 70% of the dipolar form B, but after standing for two weeks in solution at room temperature, the concentration had decreased to 35%. A CD₃OD solution contained 95% dipolar form in the fresh solution, but after one day only 50% was left. Cooling the solutions to -40°C did not change the equilibrium significantly, but the expected small shifts to lower field of the NH signal, as well as a sharpen-

ing of this signal, were observed. Only the spectrum of the two week old solution of (I) in CDCl_3 at -40°C will be considered in detail, owing to the superior quality of this spectrum.

The CH_2 signals consisted of three quartets centered at $\tau=6.50$ ppm, $\tau=6.58$ ppm, and $\tau=7.11$ ppm. By shaking with deuterium oxide the two quartets at the lowest field collapsed, indicating that these signals arise from a form in which the CH_2 protons are coupled with the NH proton. This is only possible if the NH proton is situated in a position adjacent to the CH_2 group, substantiating that this form is the dipolar form B. The coupling constant $J_{\text{NH}-\text{CH}_2}=6.0$ Hz, *i.e.* the spacing between the two quartets at the lowest field, is consistent with values found for related compounds.^{5,8,9}

The CH_2 quartet at the highest field remained unchanged on deuteration, indicating a form in which the CH_2 protons do not couple with the NH proton. The pattern arising from the NH and CH protons was a decisive factor in judging whether this form was that of either of the non-polar forms C or D. In the low-field region there were two doublets at $\tau=0.56$ ppm and $\tau=0.04$ ppm with the same spacing ($J=13$ Hz). By shaking with deuterium oxide, the doublet at the lowest field disappeared and the other collapsed. This shows that the doublet at the lowest field is the NH signal, and the other the CH signal. Moreover, it proves that the two protons are coupled, with a coupling constant of $J=13$ Hz. Finally, the non-polar form is the *trans* form C, as the *cis* form D would have a coupling constant less than *ca.* 2 Hz.⁵ The same region displayed a singlet at $\tau=0.50$ ppm, arising from the CH proton of the dipolar form and a poorly resolved signal at $\tau=-1.33$ ppm. The position of the latter peak indicates that it arises from the NH proton of form B, the signal of which is expected to occur at a lower field than the NH signal from C. These assignments were proved by deuteration. The CH_3 signals occurred as two triplets centered at $\tau=8.60$ ppm and $\tau=8.87$ ppm. Both remained unchanged on deuteration and exhibited a coupling constant of 7.0 Hz identical with the value observed for the quartets. The intensity of the triplet at the highest field increased on leaving the solution to stand and was accordingly assigned to the nonpolar form C. The same relative positions of such methyl signals have also been

observed in the spectra of related compounds (*e.g.* thioacyl-*N,N*-diisopropylhydrazines).⁵

Experimental. Conditions and equipment used for the physical measurements were those described in part I and II of this series.^{7,8}

Formyl-N,N-diethylhydrazine was prepared following the method b. given for formyl *N,N*-dibutylhydrazine by Brederick *et al.*⁹ The yield was 73 % of a colourless crystalline compound with m.p. $90-91^\circ\text{C}$ after recrystallization from ethyl acetate.

Thioformyl-N,N-diethylhydrazine (I) was prepared following essentially the method of Brederick *et al.*¹ To get an acceptable yield of pure compound it was, however, necessary to change the amount of phosphorus pentasulfide. A solution of formyl-*N,N*-diethylhydrazine (4.6 g) in dry benzene (40 ml) was treated with phosphorus pentasulfide (2.8 g). The suspension was stirred at 80°C for 7 h. After filtration of the hot mixture, the solvent was removed *in vacuo* and the residue (53 % yield) was recrystallized first from ethyl formate and then from methanol. The yield was *ca.* 5 % of a colourless, crystalline compound with m.p. $104-105^\circ\text{C}$. A similar yield was obtained by treating formyl-*N,N*-diethylhydrazine (4.6 g) with phosphorus pentasulfide (2.2 g), isolating the crude product (*ca.* 3.4 g), and treating it once more with phosphorus pentasulfide (1.6 g) following the above procedure. Treatment with phosphorus pentasulfide (3.8 g) in one step did not give a satisfactory yield. (Found: C 45.50; H 8.96; N 21.00. Calc. for $\text{C}_5\text{H}_{12}\text{N}_2\text{S}$: C 45.42; H 9.15; N 21.19). (Brederick obtained 61 % of the crude product, m.p. $80-100^\circ\text{C}$, which could be purified from ethyl formate to a m.p. of $100-105^\circ\text{C}$).

Note added in proof. In a partly overlapping investigation appearing while this paper was in press, Walter, W. and Reubke, K. *Chem. Ber.* **102** (1969) 2117, also concluded (I) prepared according to Brederick *et al.*¹ to be a dipolar rather than a thiol form.

1. Brederick, H., Fölisch, B. and Walz, K. *Ann.* **688** (1965) 93.
2. Jensen, K. A. and Nielsen, P. H. *Acta Chem. Scand.* **20** (1966) 597.
3. Bellamy, L. J. *The Infra-Red Spectra of Complex Molecules*, 2nd Ed., Methuen and Co., London 1958.
4. Ebsworth, E. A. V. and Sheppard, N. *Spectrochim. Acta* **13** (1959) 261.

5. Anthoni, U., Larsen, Ch. and Nielsen, P. H. *Acta Chem. Scand.* **23** (1969). *In press.*
6. Anthoni, U., Larsen, Ch. and Nielsen, P. H. *Acta Chem. Scand.* **23** (1969). *In press.*
7. Anthoni, U., Larsen, Ch. and Nielsen, P. H. *Acta Chem. Scand.* **22** (1968) 1025.
8. Anthoni, U., Larsen, Ch. and Nielsen, P. H. *Acta Chem. Scand.* **23** (1969). *In press.*
9. Bredereck, H., Fölisch, B. and Walz, K. *Ann.* **686** (1965) 92.

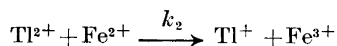
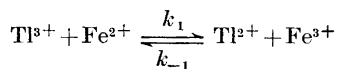
Received April 30, 1969.

Outer Sphere Electron Transfer through Substituted Pyridines

P. H. JANSEN and J. ULSTRUP

Chemistry Department A, Building 207, The Technical University of Denmark, 2800 Lyngby, Denmark

In an earlier communication¹ it was shown that in perchloric acid solution the second step of the two-step redox reaction²



is strongly catalyzed by 2- and 4-aminopyridine, but not by 3-aminopyridine. The catalytic effect was interpreted as an outer-sphere remote attack mechanism in the $\text{Tl}^{2+} - \text{Fe}^{2+}$ reaction where an electron was assumed to be transferred through the pyridine in a manner similar to that occurring in heterogeneous catalysis by bright platinum.^{3,4}

We report here evidence that 2-hydroxypyridine (2-hp) has a similar but more pronounced catalytic effect, while 3-hydroxypyridine (3-hp), like 3-aminopyridine, produces a slight retardation of the overall reaction.

The reaction was followed, at 25°C, an ionic strength of 1.60 M in perchlorate and at $[\text{H}^+] = 0.500$ M, by the procedure described earlier for experiments in the presence of 3-aminopyridine.¹ The figure shows second-order plots in the absence of a catalyst, in the presence of

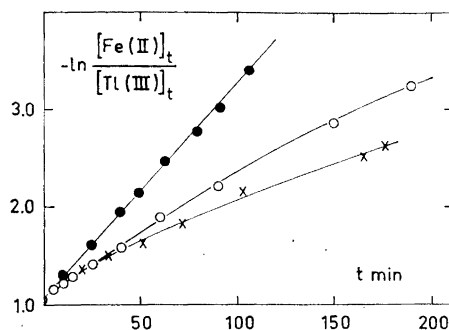


Fig. 1. Simple second-order plot. $[\text{Tl}^{3+}]_0 = 6.83 \times 10^{-3}$ M, $[\text{Fe}^{2+}]_0 = 4.76 \times 10^{-3}$ M, $[\text{Tl}^+]_0 = 1.33 \times 10^{-3}$ M. \circ no catalyst added, \bullet 0.021 M 2-hydroxypyridine, \times 0.054 M 3-hydroxypyridine.

0.021 M 2-hp, and in the presence of 0.054 M 3-hp. Straight lines are obtained for $[2\text{-hp}] \gtrsim 0.01$ M, corresponding to $k_2 \gg k_{-1}$. Also, k_1 increases with increasing $[2\text{-hp}]$, in contrast to what is observed in the presence of the aminopyridines and bright platinum, where k_1 is unaffected by the electron mediator. The rate constant of the reaction through the activated complex containing 2-hp has a value of 4.5 l/mole min, while that of Tl^{3+} and TlOH^{2+} are 0.33 and 9.4 l/mole min, respectively.

Addition of 3-hp results in a minor decrease in k_1 and k_2/k_{-1} , presumably due to the formation of complexes with Tl^{3+} , more inert than the aquo ion. This is similar to the effect of 3-aminopyridine.

The complex formation of 2-hp with Tl^{3+} , Fe^{3+} , and Fe^{2+} was measured by the same procedure as used earlier.¹ Within the limits of experimental error, no interaction was found with Fe^{2+} or Fe^{3+} , while a stability constant of 16 was found for the $\text{Tl}(\text{III})$ complex. Although the exact composition of the complex can not be stated from the present investigation, the value of the constant shows that the observed catalysis results from a very small amount of complex formation.

3-hp exists predominantly in the hydroxyform I, and in strongly acid solution as the protonated species II.⁵ No system of conjugated double bonds exists in an exchange path through the molecule, and in acid solution the free electron pair at the N-atom is not available