tions of olefins (*e.g.*, isobutylene) using t-BuCl–Me$_3$Al initiator–coinitiator systems do not proceed or proceed only with difficulty in nonpolar solvents such as n-pentane or cyclopentane. However, in methyl chloride high rates of polymerizations can be obtained.[3,4] Therefore, we conclude that similar to the alkylation model reaction, the function of methyl chloride in polymerization systems is to open the trimethylaluminum dimer and thus increase the rate of formation of the active cationic species. In addition, the polar methyl halide solvents also provide a favorable solvating medium for ion formation and separation.[15]

Experimental Section

All experiments were performed in a stainless steel enclosure under N$_2$ atmosphere (<50 ppm moisture).[13] Trimethylaluminum, triethylaluminum (Texas Alkyl Co.), and other chemicals were commercially available materials (Matheson Coleman and Bell) and were freshly distilled before use. Nmr analyses were done on Varian A-60 or T-60 instruments equipped with a low temperature probe. Optical rotation measurements were carried out using a Rudolph photoelectric Model 200 polarimeter.

Rate studies were carried out in nmr tubes and a representative procedure is described. Separate molar solutions of *tert*-butyl chloride and trimethylaluminum were prepared in methyl chloride at −60°. Trimethylaluminum solution (0.5 ml) was placed in an nmr tube and frozen in liquid N$_2$. An equal volume of the *tert*-butyl chloride solution was added to the tube and the tube was capped and sealed *in vacuo*. Subsequently, the nmr tubes were warmed up to ∼−90° to liquefy the reactants, mixed, and placed in the nmr probe maintained at a preselected temperature. Temperature equilibrium was generally established within 60 sec, at which instance the zero time was marked. The extent of the reaction was followed by observing the increase in the intensity of neopentane protons and the decrease in the intensity of protons in *tert*-butyl chloride. In general, all rate measurements were done in duplicate.

α-Phenethyl alcohol, $\alpha^{23}\text{D}$ +36° (l = 1, neat), 84% optically pure (available commercially from Norse Laboratories, Calif.), was converted to the corresponding chloride using phosphorus oxychloride, pyridine, and tetra-n-butylammonium chloride in methylene chloride at −20° in 65% overall yield.[16] The α-phenethyl chloride, bp 58–59° (5 mm) (lit.[17] bp 68° (8 mm)) had a rotation $\alpha^{23}\text{D}$ −75.1° (l = 1, neat) (corrected for optically pure alcohol[18] $\alpha^{23}\text{D}$ −92°). The nmr spectrum (CCl$_4$, δ) showed a singlet at 7.3 (aromatic, 5 H), a quartet centered at 5.0 (methine, 1 H), and a doublet at 1.8 (methyl, 3 H).

Reaction of (−)-α-Phenethyl Chloride with Triethylaluminum. In a three-necked round-bottom flask equipped with a glass-jacketed addition funnel, thermometer, and stirrer and cooled to −65° was placed 26.5 g (0.115 mol) of triethylaluminum dissolved in 200 ml of ethyl chloride. (−)-α-Phenethyl chloride, 16.1 g (0.115 mol), was dissolved in 200 ml of ethyl chloride and added dropwise through the precooled addition funnel. After 15 min stirring, the reaction was quenched by the addition of 25 ml of prechilled methanol. The aluminum methoxide was coagulated using a saturated aqueous solution of potassium sodium tartrate and the organic material was extracted into n-pentane. The pentane extract was washed three times with water and dried over anhydrous sodium sulfate. After removal of solvent, the product was distilled under reduced pressure. Initial fractions consisting mainly of ethylbenzene were discarded and the fraction boiling at 53–54° (13 mm) was collected. Its nmr spectrum (CCl$_4$, δ) showed a singlet at 7.1 (aromatic, 5 H), a sextet at 2.56 (methine, 1 H), a quartet at 1.5 (methylene, 2 H), a doublet at 1.22 (methyl, 3 H), and a triplet at 0.8 (methyl, 3 H), consistent with the structure for 2-phenylbutane. The product had a rotation $\alpha^{23}\text{D}$ −0.69° (l = 1, neat) corresponding to a net retention of 4%.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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[15] The possibility that in methyl halide solvents the actual alkylating (and propagating) intermediate is a *tert*-butyl methyl halonium ion (t-Bu-X$^+$-Me) cannot be ruled out: G. A. Olah and J. R. DeMember, *ibid.*, **91**, 2113 (1969); **92**, 718 (1970).

[16] H. M. R. Hoffman and E. D. Hughes, *J. Chem. Soc. B*, 1244 (1964).

[17] R. L. Burwell, A. D. Shields, and H. Hart, *J. Amer. Chem. Soc.*, **76**, 908 (1954).

[18] P. Harrison, J. Kenyon, and J. Shepherd, *J. Chem. Soc.*, 658 (1926).

Reversible Dimerization and Some Solid-State Properties of Two Bicyclic Nitroxides[1]

G. D. Mendenhall[2] and K. U. Ingold*

Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Canada. Received February 21, 1973

Abstract: In isopentane at 25° a 0.1 *M* solution of nortropane *N*-oxyl (**1**) contains 0.0618 *M* of the free radical and a 0.1 *M* solution of 9-azabicyclo[3.3.1]nonane *N*-oxyl (**4**) contains 0.0854 *M* of radical. Measurements at lower temperatures show that the thermodynamic parameters for the dimerization of these two nitroxides are very similar. However, the solid-state properties of **1** and **4** show striking differences. Thus, at room temperature **1** is yellow, diamagnetic, and has a strong band in its infrared spectrum attributable to the NO group at 1332 cm^{-1} in KBr. In contrast, **4** is red, paramagnetic, and has only a few weak bands in this region.

The reversible coupling of free radicals in solution to yield diamagnetic dimers is a feature common to such diverse organic radicals as triarylmethyls,[3] phenoxys,[4] alkylperoxys,[5,6] and iminoxys.[7] A few of the many stable nitroxides that are known[3] also dimerize

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[1] Issued as National Research Council of Canada No. 13420.

[2] National Research Council of Canada Postdoctorate Fellow, 1971–1973.

[3] A. R. Forrester, J. M. Hay, and R. H. Thomson, "Organic Chemistry of Stable Free Radicals," Academic Press, London, 1968.

[4] S. A. Weiner and L. R. Mahoney, *J. Amer. Chem. Soc.*, **94**, 5029 (1972).

[5] P. D. Bartlett and G. Guaraldi, *ibid.*, **89**, 4799 (1967).

[6] J. A. Howard, *Advan. Free-Radical Chem.*, **4**, 49 (1972).

[7] J. L. Brokenshire, J. R. Roberts, and K. U. Ingold, *J. Amer. Chem. Soc.*, **94**, 7040 (1972).

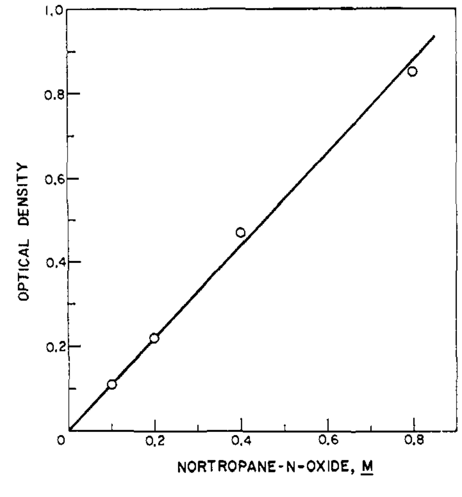
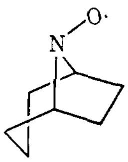


Figure 1. Beer's law for **1** in benzene at 478 nm.

reversibly in solution, *e.g.*, bis(trifluoromethyl) nitroxide[8] and tetraphenylpyrrole nitroxide.[9] The geometry of these nitroxide dimers and the nature of the bond or bonds linking the two radicals have not been determined. However, it has been shown by X-ray analysis that in one form of Fremy's salt, $(KSO_3)_2NO\cdot$, the diamagnetic crystalline form contains the two NO groups in a four-center bond.[10] A similar arrangement of the NO groups has been found for crystals of the bicyclic nitroxide, norpseudopelletierine *N*-oxyl.[11]

We have prepared the bicyclic nitroxides **1–4** in



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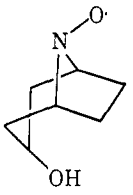

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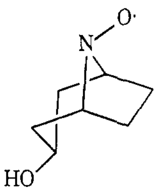

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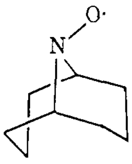

4

order to investigate some of the chemical and physical properties of unhindered stable nitroxides. To evaluate some of the results, it was necessary to know the amount of free radical present in solutions of these compounds. Our initial data[12] indicated that nortropane *N*-oxyl (**1**) was largely dimerized in isopentane at 25° at concentrations where we subsequently found that (a) the molecular weight in benzene (133 ± 6) corresponded to the monomer (126), and (b) the optical density at 478 nm in the same solvent obeyed Beer's law (Figure 1). In the present paper we show that **1** does indeed dimerize in saturated hydrocarbon solvents but that the monomer–dimer equilibrium constant, K_{eq}, is considerably greater than was indicated initially.

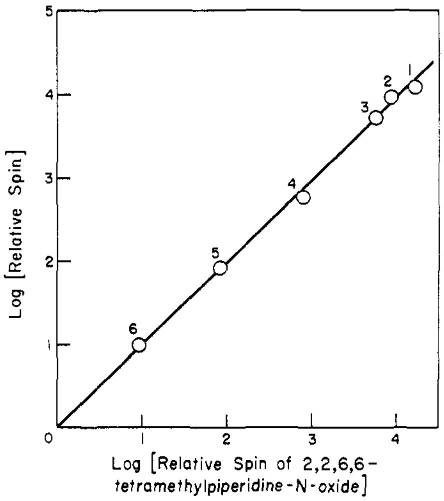

Figure 2. Plot of second integral of **1** *vs.* that of the monomeric standard in benzene at 25°. The concentrations of **1** were: for point 1, 0.625; 2, 0.313; 3, 0.16; 4, 0.025; 5, 0.0025; 6, 0.00025 *M*. The concentration of the standard was 0.555 *M* for point 1, and for each point the value of its double integral was multiplied by 0.625/0.555 = 1.13.

$$2R_2NO\cdot \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (R_2NO)_2$$

$$K_{eq} = k_{-1}/k_1$$

Results

Reversible Dimerization in Solution. An epr experiment in benzene was carried out first to see if the dimerization of **1** could be detected at all. A concentrated solution of **1** in benzene was prepared and the doubly integrated epr signal was recorded. The sample was diluted successively with pure solvent and the signal was recorded after each dilution. The procedure was then repeated with a benzene solution of 2,2,6,6-tetramethylpiperidine *N*-oxyl, a free radical that does not appear to dimerize under any conditions. A plot of the two sets of data (corrected to the same radical concentrations) appears in Figure 2. Any significant dimerization of **1** would have appeared as a downward curvature in this plot. It can be estimated from these data that K_{eq} is not less than 2 *M* at 25°. To see if the solvent could account for the difference from the value of 0.009 *M* obtained in isopentane,[12] a similar experiment was carried out in heptane in which **1** is less soluble than it is in benzene. (Heptane was chosen because it is less volatile than isopentane.) The resulting data are shown in Figure 3 and indicate that no more than a small degree of dimerization takes place at 25°.

The earlier low temperature experiments[12] were therefore repeated. Dilute solutions of **1** in isopentane were prepared and the doubly integrated epr spectrum was recorded as a function of temperature between 25 and −130°. The spectrum of a 2,2,6,6-tetramethylpiperidine *N*-oxyl solution was recorded in the same way, and the results were used to correct the double integrals of **1** for changes in signal strength due to Boltzmann and other factors. The corrected intensity of the signal due to **1** increased and decreased reversibly as the temperature was raised and lowered. The possibility that this was due to crystallization of **1** at low temperatures (single crystals are diamagnetic) and re-

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(8) W. D. Blackley and R. R. Reinhard, *J. Amer. Chem. Soc.*, **87**, 802 (1965).

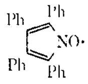
(9) R. Ramasseul, A. Rassat, G. Rio, and M.-J. Scholl, *Bull. Soc. Chim. Fr.*, 215 (1971).

(10) R. A. Howie, L. S. D. Glasser, and W. Moser, *J. Chem. Soc. A*, 3043 (1968).

(11) A. Capiomont, B. Chion, and J. Lajzerowicz, *Acta Crystallogr., Sect. B*, 27, 322 (1971). This radical has the same structure as **4** except that the two hydrogen atoms on C-3 have been replaced by a carbonyl oxygen.

(12) (a) K. Adamic, D. F. Bowman, T. Gillan, and K. U. Ingold, *J. Amer. Chem. Soc.*, **93**, 902 (1971); (b) D. F. Bowman, T. Gillan, and K. U. Ingold, *ibid.*, **93**, 6555 (1971).

Table I. Thermodynamic Parameters for Nitroxide Dimerization[a]

Radical	Solvent	$K_{eq}^{25°}/M$	ΔH, kcal/mol	ΔS, gibbs/mol	Ref
1	Isopentane	0.009[b]	7.2[b]	14.8[b]	12
1	Isopentane	0.2 ± 0.1	8.2 ± 0.3	25 ± 2	This work
1	CF_2Cl_2	0.007[b]	2.9[b]	−0.2[b]	12
1	$CFCl_3$[c]	0.5 ± 0.2	5.6 ± 0.3	17.5 ± 2	This work
1	CCl_4	0.9 ± 0.4[d]			This work
4	Isopentane	1.0 ± 0.3	8.5 ± 0.4	28.6 ± 2	This work
$(CH_3CD_2)_2NO\cdot$	Isopentane	0.63	7.6	24.8	12
$(CH_3CD_2)_2NO\cdot$	CF_2Cl_2	0.018	2.6	0.1	12
$(CH_3CH_2)_2NO\cdot$	CF_2Cl_2	0.34	6 ± 3	18 ± 20	12
$(CF_3)_2NO\cdot$	CF_2Cl_2	0.45 ± 0.1	2.4 ± 0.3	6.5 ± 2	8
	CH_2Cl_2	0.001	13	30	9
$(CH_3)_3COO\cdot$	Isopentane	2.5	8.4 ± 0.4	30	6

[a] Errors obtained from lines of maximum and minimum slope that fit the data acceptably. [b] Sample probably impure. See text. [c] Containing 10% isopentane. [d] Single determination at 25° by the method of Figure 2 with the formal concentration of **1** = 0.24 *M*.

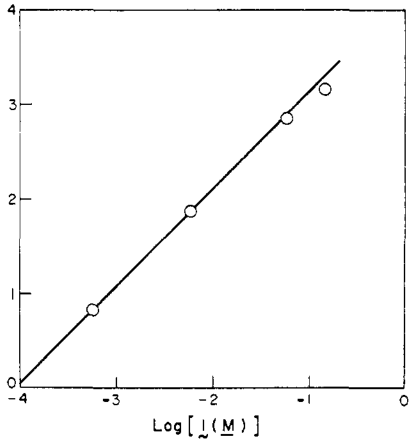


Figure 3. Plot of second integral of **1** *vs.* its concentration in heptane at 25°.

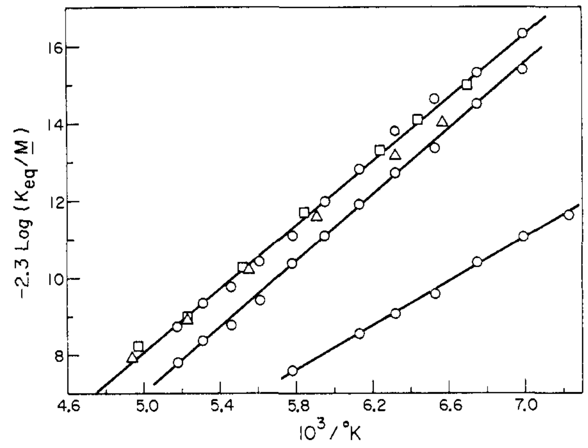


Figure 4. The reversible dimerization of **1** and **4** as a function of temperature. $M_0 \times 10^4$: top, **1** in isopentane (△) 3.5, (○) 3.3, (□) 1.1; middle, **4** in isopentane (○) 3.9; bottom, **1** in $CFCl_3$–10% isopentane (○) 1.9.

dissolution on warming was eliminated as follows. A concentrated solution of **1** in isopentane was cooled to −158° and filtered at this temperature. The filtrate was warmed to 25° and the epr signal intensity due to **1** was measured. The solubility at −158° (0.0004 *M*) determined in this way was higher than the concentrations of **1** used in the variable temperature experiments. It must therefore be concluded that in isopentane **1** dimerizes at low temperatures as we originally reported.[12] Reproducible equilibrium constants were obtained between −70 and −130° with solutions $\geqslant 10^{-4}$ *M* in **1** (see Figure 4). At a lower concentration (3.6×10^{-5} *M*) the calculated equilibrium constants were smaller and showed less variation with temperature. This result is probably due to a systematic error in determining low radical concentrations because of small background signals in the epr cavity. The possibility that at the higher concentrations **1** forms diamagnetic species containing more than two radicals cannot, however, be entirely ruled out.

The dimerizations of **1** in $CFCl_3$ (containing 10% isopentane to lower its freezing point) and of 9-azabicyclo[3.3.1]nonane *N*-oxyl (**4**) in isopentane were examined in the same way. The data for all the nitroxides were analyzed according to the equation

$$K_{eq} = 2x^2M_0/(f - x)$$

where M_0 is the formula weight concentration of radical at 25°, M is the measured radical concentration, $x = M/M_0$, and $f = d^T/d^{25}$, the ratio of densities of the solution at T and 25°. Values for the equilibrium constant at 25° and for ΔH and ΔS calculated from the van't Hoff relation are given in Table I together with the data from previous work which were calculated with $f = 1$.

Solid-State Properties of 1 and 4. Striking differences were observed in the physical properties of crystalline samples of these radicals. Regular, single crystals of **1** were mounted on a goniometer and placed in the epr spectrometer cavity. A weak *triplet* was the only signal observed. Since the signal was orientation independent and remained when the crystal was removed, it is ascribed to a small concentration of radical that must have diffused into the fluorolube mounting grease. Irregular crystals of **1**, however, gave relatively strong asymmetric signals with three or four maxima depending on the orientation of the conglomerate within the cavity.

All solid samples of the homolog, **4**, displayed a single strong line with a *g* factor near the free-spin value. The signal is very narrow (half-width < 5 G) presumably because of rapid spin exchange.[13]

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[13] T. A. Miller and R. N. Adams, *J. Amer. Chem. Soc.*, **88**, 5713 (1966).

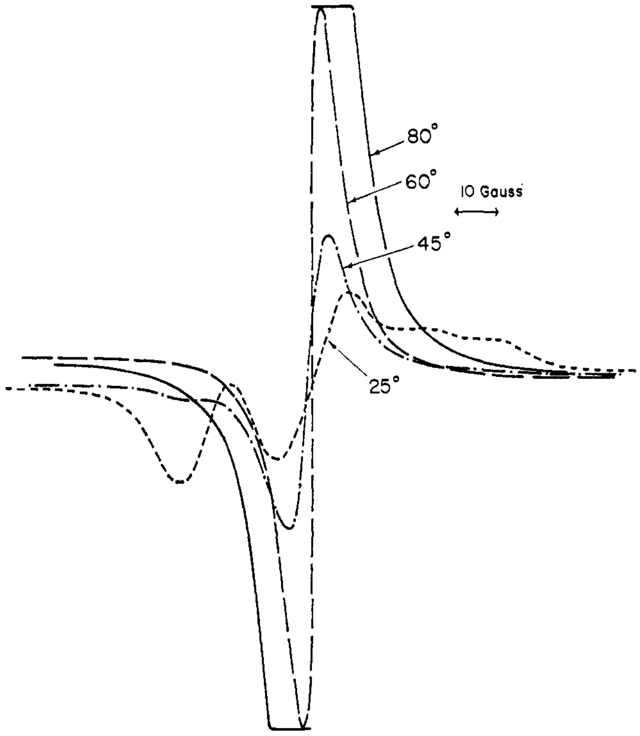

Figure 5. Change in the epr spectrum of powdered **1** with temperature. Receiver gain = 10^4 at 25°; 10^3 at 45°; 10^2 at 60 and 80°.

Small samples of **1** and **4** were ground up with potassium chloride and the epr signals were examined at different temperatures. The double integrals were corrected for the Boltzmann factor with 5.7×10^{-5} *m* DPPH in KCl integrated under the same conditions. The results (Table II) show that **1**, but not **4**, undergoes spin pairing at the lower temperatures.

Table II. Relative Spin Intensities for **1** and **4** (*ca.* 10^{-4} *m*) at Different Temperatures in KCl

Temp, °C	Relative spin[a] **1**	Relative spin[a] **4**
25	1.0	1.0
−100	0.51	1.3
−175	0.44	1.7

[a] Corrected for temperature dependence with DPPH in KCl. Probable error = ±30%.

All four nitroxides displayed thermochromic behavior. The yellow colors of **1**, **2**, and **3** were distinctly less intense at −20° than at room temperature and disappeared completely at −196°. Compound **1** undergoes a phase transition to yield pale red crystals at 74°. Sublimation to this form also occurs at lower temperatures. However, the ground-up sample of **1** in KCl remained only weakly paramagnetic up to 130° with no distinct changes at the phase transition or at the melting point, 130°. In contrast to **1**, compound **4** remains deep red even at −196°. It undergoes a phase transition at 54° to a yellow modification and a second transition (which is more rapid than the first and is observed individually in each crystal) at about 70° to give pale red crystals that melt to a red liquid above 130°.

Because the two radicals might have sublimed out of the KCl at high temperatures, pure, powdered solid samples of **1** and **4** were sealed in small capillary tubes and examined at different temperatures. Nitroxide **1** now showed a weak signal at 25° resembling a powder spectrum. This was overshadowed above 45° by a single narrow line that became many orders of magnitude more intense at 80° (Figure 5) at which temperature the sample was red. On cooling to 25° the original yellow color was restored immediately, but the intense epr singlet signal required about 8 hr to decay completely. Radicals **2** and **3** showed similar behavior on warming above 80°, but in these cases the signal increase and red coloration were associated with the impure samples partially melting rather than with phase changes in the solids.

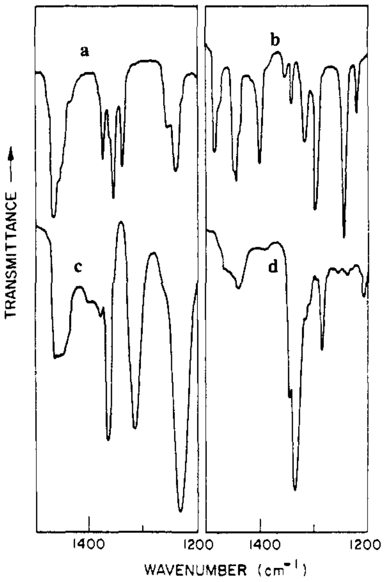

Figure 6. Infrared spectra of 0.012 *m* nitroxides in KBr disks: (A) 2,2,6,6-tetramethylpiperidine *N*-oxyl; (B) 4-keto derivative of A; (C) **4**; (D) **1**.

The epr spectrum of solid **4** at 25° was a strong singlet that *decreased* irreversibly in intensity by a factor of about 2 between 45 and 60° (*i.e.*, above the first phase transition). No further gross change was noted on warming the sample above the temperature of the second phase transition. None of the solid nitroxides exhibited the complex temperature-dependent epr spectrum observed with Fremy's salt and attributed to the presence of a thermally accessible triplet state.[14]

The infrared spectra in paraffin mulls of **1**, **2**, **3**, and nortropinone *N*-oxyl all have strong absorptions in the 1332–1345-cm^{-1} region which is about 30 cm^{-1} lower than the absorption bands attributed to the NO group for several hindered nitroxides in carbon disulfide.[15] In contrast, the spectrum of **4** displays only weak bands in this region and assignment to the NO group is uncertain. It would appear that although a band at 1350 ± 25 cm^{-1} may indicate the presence of a nitroxide (or its dimer), the intensity of the band is so variable even for structurally related radicals that it is of limited diagnostic value. This point is further illustrated by Figure 6 which shows the infrared spectra in

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(14) B. D. Perlson and D. B. Russell, *J. Chem. Soc., Chem. Commun.*, 69 (1972).

(15) C. Morat and A. Rassat, *Tetrahedron*, **28**, 735 (1972). We could not obtain the spectrum of **1** in CS_2 because it reacted with this solvent. The NO band for $t\text{-}Bu_2NO\cdot$ is at 1345 cm^{-1}: A. K. Hoffman and A. T. Henderson, *J. Amer. Chem. Soc.*, **83**, 4671 (1961).

KBr discs of **1** and **4** and of 2,2,6,6-tetramethylpiperidine *N*-oxyl and its 4-keto derivative.

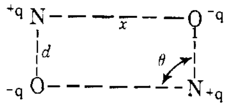
Discussion

In isopentane, which is a "poor" solvent for nitroxide and dimer[12] since it is both nonpolar and nonpolarizable, the thermodynamic parameters found for the reversible dimerization of **1**, **4**, and $(CH_3CD_2)_2NO\cdot$ are very similar. The much lower equilibrium constant and ΔS value reported previously for **1** may well have been due to measurements on an impure sample since we had not realized at that time that **1** is not very stable.[16] In more polar and polarizable solvents such as $CFCl_3$ and CF_2Cl_2 the enthalpy and entropy of dimerization decrease because the radicals are more strongly solvated (because of their dipolar character) than the dimer.[12]

We expect little difference between heptane and isopentane as solvents, and the extrapolated value of K_{eq} obtained from low-temperature measurements accounts for the negative deviation just detectable at the higher concentrations at 25° in Figure 3. Calculations indicate that the vertical deviation of the highest point from the line should actually be about twice that observed, but this discrepancy is well within the experimental errors of the two procedures.

It is interesting to note that the thermodynamic parameters for nitroxide dimerization in isopentane are similar to those for *tert*-alkylperoxy dimerizations in alkane solvents[6] (*e.g.*, *tert*-butylperoxy in isopentane, see Table I). In the latter case a classical tetroxide structure, ROOOOR, is preferred as it readily explains the decomposition of the dimer to two *tert*-alkoxy radicals and oxygen. A similar structure for nitroxides, *i.e.*, R_2NOONR_2, is unlikely on thermodynamic grounds.[12b]

While the structure of nitroxide dimers in solution is uncertain, we may estimate the dipolar attractive force between two nitroxides by a point charge calculation similar to that used originally for calculating the strengths of hydrogen bonds.[17,18] It is assumed that the dimer has a four-center bond with the same dimensions as those reported for crystalline norpseudopelletierine *N*-oxyl,[11] *viz.*



$d = 1.289$ Å

$x = 2.278$ Å

$\theta = 89.9°$

For this structure, if θ is taken to be 90°, the dipolar attractive force is given by

$$E = \frac{Lq^2}{x\epsilon}\left(\frac{1}{(1 + d^2/x^2)^{1/2}} - 1\right)$$

Taking $L = 6.0226 \times 10^{23}$ mol^{-1}, $\epsilon = 1$, and giving q the value (2.43×10^{-10} esu or 0.506 e) required to obtain the bulk dipole moment of 3.14 D reported for 2,2,6,6-tetramethylpiperidine *N*-oxyl[19] gives $E = 4.9$ kcal/mol. Although this solution involves some rather gross assumptions, it is interesting to find that dipolar attraction can provide a very significant fraction of the enthalpy for dimerization of unhindered nitroxides in solution.

Compounds that can form intermolecular hydrogen bonds virtually always crystallize in such a way as to preserve them.[20] In the case of the nitroxides **1** and **4** the orientation required to form dimer pairs must be so strict that subtle energetic factors of crystal packing override the driving force toward dimerization in **4**, though not in **1**.

Empirically we note that at 25° **1**, **2**, **3**, and nortropinone *N*-oxyl[21] are yellow and diamagnetic, whereas **4**, a nitroxide derived from **4** and Ag_2O,[16] and most hindered nitroxides are red and paramagnetic. At room temperature irregular crystals or ground samples of **1** contain enough radicals to give an epr signal. Some of these radicals are sufficiently mobile to pair up at lower temperatures (Table II). The decrease in the intensity of the yellow color of **1** on cooling cannot be due to this spin pairing since diamagnetic single crystals of **1** are also decolorized on cooling. It is, however, tempting to associate the red color of **1** at temperatures above 74° with the strong epr signal, *i.e.*, with monomeric **1**. The hysteresis of the epr signal on cooling may be due to a slow change of a few recalcitrant crystals containing mostly monomeric **1** or to a slow pairing of individual radicals spread throughout the diamagnetic mass. These intriguing phenomena could probably be studied more profitably by X-ray and other techniques.

Experimental Section

The preparation of the radicals for this investigation is described in the following paper.[16]

The solubility of **1** in isopentane was determined in an argon-flushed, serum-capped U-tube with a fine glass frit at the bottom of the U. The lower part was immersed in an isopentane slush bath in a way that 2 cm^3 of a 0.07 *M* solution of **1**, contained in one side of the U, did not wet the glass frit. After 40 min at −158°, the apparatus was tipped and suction was applied to draw the solution into the empty chamber. A sample was withdrawn with a syringe and the concentration of **1** was determined by epr assay with a sample of the original solution as the standard.

The density of isopentane at low temperatures was calculated from a published formula.[22] The density of $CFCl_3$ containing 10% isopentane was found to increase by a factor of 1.23 on cooling from 25 to −100°. Since this is close to the increase of isopentane itself over this temperature range (1.21), we used the same f values for both solutions.

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[16] G. D. Mendenhall and K. U. Ingold, *J. Amer. Chem. Soc.*, **94**, 7166 (1972); **95**, 6395 (1973).

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