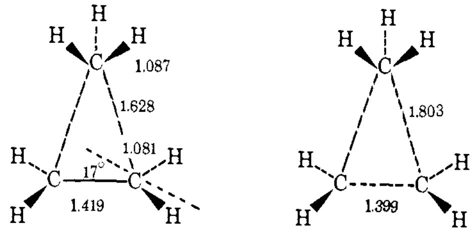
angle in I to be the same as in propane (110.5°), by assuming the methyl carbon in II to lie midway between the methylene carbons, and by assuming the central hydrogen in IV to lie midway between the carbon atoms. Apart from these restrictions, all the values reported in this communication correspond to structures optimized with respect to all geometrical parameters.

These results differ in several respects from those reported by Pople, *et al.*,[1e] using an *ab initio* SCF method. They concluded that the most stable form should be a somewhat distorted n-propyl cation, I, with a CCC bond angle of 101.5°, and that i-Pr$^+$ should be more stable than I by 20 kcal/mol. The predicted order of stability of the other isomers was I > II > III > IV.

The chemical evidence suggests that I can isomerize easily to II or III in solution, that II and III are stable in solution, and that III is probably more stable than II.[5] Since the solvation energies of the classical ions I and i-Pr$^+$ must be greater than those of the "nonclassical" ions II and III, our results seem to be in better agreement with the available evidence than those of Pople, *et al.*[1e] Our geometry for the π complex II also seems more reasonable than theirs (see Chart I). It is difficult to believe that the apical–basal CC bonds could be so much longer than the bonds in cyclopropane.

Chart I. Calculated Geometries for II[a]



a b

[a] Bond lengths in ångströms: a, MINDO/2; b, *ab initio* SCF.[1e]

Our calculations lead to the prediction that III should be more stable than i-Pr$^+$ in the gas phase though the difference in heat of formation (4 kcal/mol) is too small for this conclusion to be reliable. The fact that i-Pr$^+$ is the stable form of $C_3H_7^+$ in solution is of course irrelevant in this connection since, as pointed out above, the energy of solvation of i-Pr$^+$ must be much greater than that of III.

Since *ab initio* SCF methods give very poor estimates of heats of atomization, they can be used to calculate energies only on an empirical basis. While some justification exists for their use in comparing systems with equal numbers of similar bonds,[6] this does not extend to comparisons of dissimilar species such as I–IV. Since MINDO/2 has been shown to give good estimates of heats of atomization for a wide variety of molecules, including (see above) carbonium ions, and also activation energies for several reactions,[2,7] we feel that the results reported here may give reasonably reliable results in situations of the type considered here.

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[6] W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 4796 (1970).

[7] M. J. S. Dewar, A. Harget, and E. Haselbach, *ibid.*, **91**, 7521 (1969); M. J. S. Dewar, E. Haselbach, and M. Shansal, *ibid.*, **91**, 3506 (1969); A. Brown, M. J. S. Dewar, and W. Schoeller, *ibid.*, **92**, 5516 (1970); M. J. S. Dewar and W. W. Schoeller, *ibid.*, **93**, 1481 (1971); *Tetrahedron*, **27**, 4401 (1971).

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Self-Reactions of Diethylamino and Diisopropylamino Radicals[1]

Sir:

The chemistry of dialkylamino radicals has received little attention, and accurate kinetic and thermodynamic data for such radicals are almost nonexistent. We wish to report the first absolute rate measurements for the self-reactions of diethylamino and diisopropylamino radicals in solution. Both of these radicals (and also the dimethylamino radical) were generated in the cavity of a Varian E-3 epr spectrometer by photolysis of the appropriate tetraalkyltetrazene in a hydrocarbon solvent. The epr spectra of these radicals have been reported previously by Danen and Kensler using the same technique.[3] Decay of the radicals when the light

$$R_2N{-}N{=}N{-}NR_2 \xrightarrow{h\nu} 2R_2N\cdot + N_2$$

was cut off was monitored in the usual way.[4]

The epr signal due to dimethylamino was too weak for kinetic studies. Diethylamino radicals decayed with second-order kinetics at a rate close to the diffusion-controlled limit. In n-pentane at −90°, the decay rate constant, $k_{\mathrm{epr}}{}^2 = 2k^{\mathrm{Et_2N}}$, was $(7 \pm 3) \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$

$$2Et_2N\cdot \xrightarrow{2k^{Et_2N}} \text{nonradical products}$$

Diisopropylamino radicals decay completely with clean second-order kinetics at temperatures below ~−10°. In n-pentane, the measured decay rate constant $k_{\mathrm{epr}}{}^2 = (4.5 \pm 1.0) \times 10^6\ M^{-1}\ \mathrm{sec}^{-1}$ at all temperatures in the range −13 to −70°. If a sample of the tetrazene which has been photolyzed at these low temperatures is allowed to warm up in the dark after the i-Pr$_2$N· radical has completely decayed, the signal due to this radical reappears at ~−5° and grows rapidly as the temperature is raised further. In typical experiments, a radical concentration of $\sim 5 \times 10^{-7}\ M$ is obtained at ~+10°, and this does not decay noticeably in 20 min. In the range −5 to ~+20°, the radical concentration could be increased and decreased reversibly by raising and lowering the temperature. Presumably, the radical is in equilibrium with its dimer, tetraisopropylhydrazine.

$$2\,i\text{-}Pr_2N\cdot \rightleftharpoons i\text{-}Pr_2NN\text{-}i\text{-}Pr_2$$

The variation in radical concentration with temperature yielded a heat of formation of the dimer, $\Delta H = 25 \pm$

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[1] Issued as NRCC No. 12279. Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. IV.[2]

[2] Part III: D. F. Bowman, T. Gillan, and K. U. Ingold, *J. Amer. Chem. Soc.*, **93**, 6555 (1971).

[3] W. C. Danen and T. T. Kensler, *ibid.*, **92**, 5235 (1970).

[4] K. Adamic, D. F. Bowman, T. Gillan, and K. U. Ingold, *ibid.*, **93**, 902 (1971).

2 kcal/mol. This value is much less than the N–N bond strength in hydrazine, which has recently been estimated to be 72 kcal/mol,[5] while that in tetramethylhydrazine is apparently 53 kcal/mol.[5] The small bond strength of the isopropyl compound is presumably due to steric factors.

At 25° the thermally produced $i\text{-Pr}_2\text{N}\cdot$ radicals start to decay with *first-order* kinetics. At temperatures of 25° and above, the first-order decay rate constant, $k_{\text{epr}}{}^1$, in *n*-octane can be described by

$$k_{\text{epr}}{}^1 = 10^{14.4\pm1.2}e^{-(24000\pm2000)/RT}\ \text{sec}^{-1}$$

This expression was obeyed both by thermally produced radicals from the (assumed) hydrazine and by photochemically produced radicals from the tetrazene. In the latter case, an initial rapid decay was followed by the much slower first-order process, the decay curves showing quite sharp breaks at the point where the radical–hydrazine equilibrium is achieved. If the temperature was raised during the course of a decay, the radical concentration rose temporarily because of the shift in the equilibrium. At 70°, $k_{\text{epr}}{}^1$ was independent of the tetrazene concentration (from 0.02 to 0.2 *M*), independent of the extent of photolysis of the tetrazene, and had the same value in cyclohexane as in perdeuteriocyclohexane.

An attempt to detect tetraisopropylhydrazine by nmr was unsuccessful. A 0.6 *M* tetrazene solution in perdeuterio-*n*-heptane was photolyzed at −70°, and the nmr spectrum was examined at intervals without allowing the sample to warm up until the tetrazene was about 35% decomposed. The only detectable products were diisopropylamine and the Schiff base $i\text{-PrN}{=}\text{C(CH}_3)_2$. The sample was warmed to 40° and kept until the radical signal disappeared. There was no detectable change in the concentration of the two products, and hence the overall yield of hydrazine is small. The yield formed in the primary reaction of two diisopropylamino radicals could of course be quite high, but because the hydrazine could itself be photolyzed, its steady-state concentration would be kept low. A low steady-state hydrazine concentration is indicated by the observation that the same radical concentration was produced at 10° on warming samples that had been photolyzed at −70° for a few minutes or for 1 hr.

We have considered various possible explanations of the foregoing results on the $i\text{-Pr}_2\text{N}\cdot$ radical and believe the following decay mechanism to be most probable.

$$i\text{-Pr}_2\text{NN-}i\text{-Pr}_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\text{-}i\text{-Pr}_2\text{N}\cdot \xrightarrow{k_2} i\text{-Pr}_2\text{NH} + i\text{-PrN}{=}\text{C(CH}_3)_2$$

At low temperatures, where k_{-1} is not significant, decay is second order, with $k_1 + k_2 = k_{\text{epr}}{}^2 = 4.5 \times 10^6\ M^{-1}$ sec^{-1}. At higher temperatures, when k_{-1} becomes significant, the following kinetic analysis shows that radical decay will be first order

$$\text{d[N}\cdot]/\text{d}t = -k_1[\text{N}\cdot]^2 + k_{-1}[\text{N}_2] - k_2[\text{N}\cdot]^2$$

and

$$\text{d[N}_2]/\text{d}t = k_1[\text{N}\cdot]^2 - k_{-1}[\text{N}_2] = -\text{d[N}\cdot]/\text{d}t - k_2[\text{N}\cdot]^2$$

where $\text{N}\cdot$ refers to the radical and N_2 to the hydrazine. Provided $[\text{N}\cdot] \ll [\text{N}_2]$, then $\text{d[N}\cdot]/\text{d}t \ll \text{d[N}_2]/\text{d}t$ and hence

$$\text{d[N}_2]/\text{d}t = -k_2[\text{N}\cdot]^2 \qquad (1)$$

Now, if $k_1 > k_2$, then $k_{-1}[\text{N}_2] \approx k_1[\text{N}\cdot]^2$ and therefore

$$\text{d[N}_2]/\text{d}t = (2k_1/k_{-1})[\text{N}\cdot]\text{d[N}\cdot]/\text{d}t \qquad (2)$$

Combining eq 1 and 2 yields the first-order rate expression

$$-\text{d[N}\cdot]/\text{d}t = (k_2k_{-1}/2k_1)[\text{N}\cdot]$$

The most probable alternative reaction scheme involves formation of the amine and Schiff base by a direct molecular decomposition of the hydrazine, rate constant k_3 (*cf.* ref 5). Making similar assumptions, the resulting kinetic expression[6] is

$$-\text{d[N}\cdot]/\text{d}t = k_3[\text{N}\cdot]/2$$

This possibility cannot be ruled out, but the similarity in the values of ΔH_{-1} for dimer formation and $E_{\text{epr}}{}^1$, the activation energy for the unimolecular decay, seems to us to argue in favor of the first mechanism. That is, if $k_{\text{epr}}{}^1$ is equated with $(k_{-1}/k_1)(k_2/2)$, then

$$E_{\text{epr}}{}^1 = \Delta H_{-1} + E_2$$

from which $E_2 = -1 \pm 4$ kcal/mol. Similarly

$$A_{\text{epr}}{}^1 = e^{\Delta S_1/R}A_2/2$$

If ΔS_1 is taken to be 37 gibbs/mol (which is probably a minimum value because the hydrazine is such a hindered molecule that there must be large barriers to many of the internal rotations), then $A_2 = 10^{6.6}\ M^{-1}\ \text{sec}^{-1}$.

The foregoing results suggested to us that a di-*tert*-alkylamino radical would be too hindered to dimerize. Since it could not disproportionate, it should be "stable" in the sense that it could not undergo a bimolecular self-reaction. A unimolecular β scission is not expected to be important unless the leaving radical is resonance stabilized. Preliminary results with 2,2,6,6-tetramethylpiperidyl indicate that the above expectations are fulfilled with this radical. However, we have not, so far, discovered a solvent that is inert to this radical at room temperature. The facile abstraction of hydrogen from, for example, cyclohexane ($k^{24°} = 0.2\ M^{-1}\ \text{sec}^{-1}$) provides support for the recent revision of the N–H bond strength in $(\text{CH}_3)_2\text{NH}$ upward from 86 kcal/mol[7] to 95 kcal/mol.[5] Studies on this di-*tert*-alkylamino radical will be detailed in our full paper.

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(6) L. R. Mahoney and S. Weiner, presented at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971.

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(8) NRCC Postdoctorate Fellow, 1970–1971.

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Platinum. A Noble Metal, "Base" Atoms

Sir:

The presence of native metal from mineral sources and the failure to react with any but the strongest oxidizing agents early distinguished platinum as the most inert of the metals and earned for it the allegation of nobility.[1]

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(1) W. Lewis, *Phil. Trans. Roy. Soc. London*, **48,** 646 (1754).