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_{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_{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 $i\text{-PrN{=}C(CH}_3)_2$. 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.

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

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

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

and

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

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

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

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

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

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

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

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

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

This possibility cannot be ruled out, but the similarity in the values of ΔH_{-1} for dimer formation and E_{epr}^1, the activation energy for the unimolecular decay, seems to us to argue in favor of the first mechanism. That is, if k_{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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[5] S. W. Benson and D. M. Golden, quoted in *Chem. Eng. News*, **48**, 31 (Nov 23, 1970).

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

[7] See, *e.g.*, J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).

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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).

This noble metal is made of "base" atoms: atoms of platinum are reactive.

This might have been anticipated as follows. The high boiling point of the metal (>3800°) is evidence of very strong interaction forces. Large interaction forces saturate the combining capacity of an atom. Under these circumstances, the chemical reactivity of the bulk substance bears little resemblance to the chemical reactivity of the atoms. As evidence, the reaction at $-196°$ of carbon atoms with various substrates[2] was not predictable from the chemical properties of graphite or diamond, boiling point ~4200°. As a rough rule of thumb, the higher the boiling point of an element the less is the similarity in chemical properties of the atoms and the bulk element.

By a method similar to that employed in studying carbon atoms,[3] platinum atoms (evaporated from a tungsten filament at 1950°) were generated under high vacuum and were deposited simultaneously with a large excess of substrate on the walls of the vessel which were cooled to $-196°$. The flight to the walls was collision free, the first encounters of the platinum atoms with substrate being on the cold walls. Reaction products are separated from the large excess of substrate after completion of the deposition.

Propene reacts with platinum atoms. The excess propene was pumped away at low temperature leaving the organoplatinum compounds. Hydrolysis of this residue with water released propene, propane, 2,3-dimethylbutane, 2-methylpentane, and hexane in decreasing amounts, propene being the major hydrolysis product. These isolated products indicate that a minimum of 1.04 mmol of propene had reacted per 1.00 mmol of platinum. Hydrolysis with deuterium oxide produces propene which is mainly unlabeled. This is behavior similar to that observed with atoms of palladium[4] and nickel,[5] but quite different from that observed with aluminum,[6] chromium,[7] zirconium,[8] the lanthanides,[9] etc., wherein deuterium incorporation is high.

A similar reaction occurs with 1-butene. The excess 1-butene is not isomerized in contact with the organoplatinum compound. Isomerization is observed in a number of other metal atom systems (cobalt atoms[10] are especially effective). However, introduction of hydrogen results in catalytic uptake to produce butane.

Platinum atoms react with 1,5-cyclooctadiene. Extraction of the nonvolatile products with hexane and purification by filtration through a column of alumina leaves a colorless residue. The nmr, infrared, and mass spectra are identical with those described earlier[11] for bis(1,5-cyclooctadiene)platinum(0). This compound was isolated in 64% yield.

The product from platinum atoms and 1,3-butadiene is catalytic for the hydrogenation of the excess butadiene at $-78°$. After reaction of 400 mol of butadiene per mole of platinum, the hydrogenation reaction was stopped with 40% of the butadiene unreacted. The major product was butane; only small amounts of the isomeric butenes were present. This contrasts with the catalytic properties of the usual platinum catalysts.[12]

Allyl chloride reacts with platinum atoms. The product is a yellow solid which decomposes at 160–170° and is sparingly soluble in chloroform and benzene. This yellow compound reacts with triphenylphosphine to yield $[\mathrm{PtCl(C_3H_5)((C_6H_5)_3P)}]$, identified by its mass spectrum and decomposition range 180–190° (lit.[13] 182–188°).

Di-π-allyldi-μ-chloro-dipalladium is reported[14] to hydrolyze at 100° to 1 mol of propene, 1 mol of acrolein, 2 mol of hydrogen chloride, and 2 mol of palladium. When 72.7 mg of the platinum–allyl chloride compound is heated in water for 17 hr at 110°, acrolein, 0.126 mmol of propene, and 0.258 mmol (51.6 mg) of platinum are formed. The 2:1 ratio of platinum to propene and the weight per cent of platinum (71%) indicates that the complex has the formula $[\mathrm{Pt(C_3H_5)Cl}]_x$ (calcd, 72% Pt). The platinum–allyl chloride adduct is thought to be the known[13] tetranuclear complex $[\mathrm{PtCl(C_3H_5)}]_4$, which is reported to decompose at 173–184°. On the basis of the tentative proposal, the yield is 48%.

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The Structure of α-Cyclobutadienyliron Tricarbonyl Carbonium Ions

Sir:

The very pronounced increase in the stability of a carbonium ion following introduction of an α-organometallic substituent has been recognized for some time but the origin of the stabilization remains obscure. The effect is readily seen in the following three examples: (1) the rate of solvolysis of α-ferrocenylcarbinyl acetate is approximately equal to that of trityl acetate,[1a,b] (2) (benzyl chloride)chromium tricarbonyl solvolyzes 10^5 times faster than benzyl chloride itself,[2] and (3) as we have now found, chloromethylcyclobutadieneiron tricarbonyl solvolyzes at least 10^8 times faster than does benzyl chloride.[3] These data indicate that the cations

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[1] (a) E. A. Hill and S. H. Richards, *J. Amer. Chem. Soc.*, **81**, 3483 (1959); **83**, 3840, 4216 (1961). (b) For a review of the earlier work in the ferrocene series, see M. Cais, *Organometal. Chem. Rev.*, 1, 435 (1966).

[2] J. D. Holmes, D. A. K. Jones, and R. Pettit, *J. Organometal. Chem.*, 4, 324 (1965); R. Pettit, *Ann. N. Y. Acad. Sci.*, **125**, 89 (1965).

[3] This solvolysis rate was calculated from the rate at which chloromethylcyclobutadieneiron tricarbonyl approaches equilibrium with the alcohol in 5% aqueous acetone. The reaction was monitored by 100-MHz nmr (35°, $k_1 = 1.105 \times 10^{-2}$, $k_2 = 1.520 \times 10^{-3}$). This is a clear