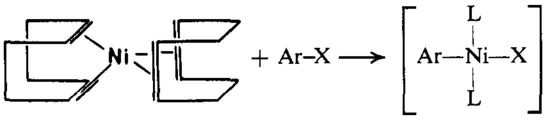
the expense of the coupling reaction. The reaction of 6-bromopiperonyl alcohol under the usual conditions affords piperonyl alcohol in 31% yield accompanied by 51% of unreacted aryl halide and none of the corresponding biaryl. This side pathway is a limitation of the aryl coupling reaction, but is under investigation as a mild and selective method of reducing aromatic carbon–halogen bonds. Removal of the proton source by forming the sodium salt (*e.g.*, entries 21 and 22 in Table I) appears to strongly deactivate the aryl halide toward coupling.

The only solvent which has been found to be satisfactory for the coupling reaction is dimethylformamide. No reaction of aryl halides and bis(1,5-cyclooctadiene)nickel occurs at moderate temperature in less polar solvents such as tetrahydrofuran or toluene; dimethyl sulfoxide and hexamethylphosphoric triamide are not useful due to rapid decomposition of the nickel reagent in these solvents.

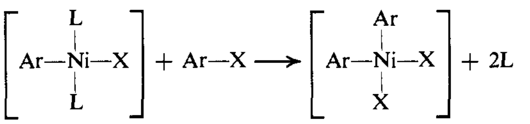
The reactivity of the aryl halides is approximately in the order I > Br > Cl; phenol *p*-toluenesulfonate esters are completely unreactive. Generally, both electron-attracting and electron-donating substituents allow efficient coupling with no significant difference in rate, but nitro groups strongly inhibit coupling. Both 2-nitro- and 4-nitrobromobenzene are recovered unreacted under the usual conditions.

A preliminary study of the mechanism of the reaction implicates a transient aryl–nickel intermediate. Under the usual conditions, iodobenzene and bis(1,5-cyclooctadiene)nickel were allowed to react in dimethylformamide while aliquots were removed at intervals, partitioned between water and pentane, and the pentane solution was analyzed by glpc. The analyses showed clearly the rapid disappearance of iodobenzene and slower formation of biphenyl. The above results are accommodated by the tentative reaction sequence of eq 2–4, in accord with recent suggestions for other metal-promoted coupling of aryl halides,[1] and the general theory of oxidative addition to low-valent transition metals.[10] Alternative pathways *via* direct bimolecular reaction of an arylnickel halide with an aryl halide or *via* free-radical intermediates cannot be excluded at this time.



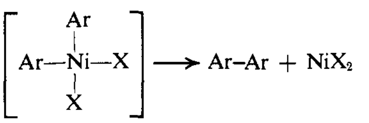
(2)

L = solvent or COD



(3)

$$\left[\begin{array}{c}\mathrm{L}\\ |\\ \mathrm{Ar{-}Ni{-}X}\\ |\\ \mathrm{L}\end{array}\right] + \mathrm{Ar{-}X} \longrightarrow \left[\begin{array}{c}\mathrm{Ar}\\ |\\ \mathrm{Ar{-}Ni{-}X}\\ |\\ \mathrm{X}\end{array}\right] + 2\mathrm{L} \qquad (3)$$



(4)

$$\left[\begin{array}{c}\mathrm{Ar}\\ |\\ \mathrm{Ar{-}Ni{-}X}\\ |\\ \mathrm{X}\end{array}\right] \longrightarrow \mathrm{Ar{-}Ar} + \mathrm{NiX_2} \qquad (4)$$

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The Mechanism of Azoalkane Fragmentation

Sir:

Azoalkanes have been used for many years as a convenient source of alkyl radicals, and for almost as many years chemists have pondered details of the initial reaction.[1] Two schemes have been dominant, and a choice has been made more often than proven. A review presenting a strong case for the formation of three fragments in the rate-determining step (eq 1) has recently appeared.[2]

$$\mathrm{R{-}N{=}N{-}R'} \longrightarrow \mathrm{R\cdot} + \mathrm{N_2} + \mathrm{\cdot R'} \qquad (1)$$

Almost simultaneously the alternative two-fragment process (eq 2) has been supported in the literature by an

$$\mathrm{R{-}N{=}N{-}R'} \longrightarrow \mathrm{R\cdot} + \mathrm{\cdot N{=}N{-}R'} \xrightarrow{\text{fast}} \mathrm{N_2} + \mathrm{\cdot R'} \qquad (2)$$

analysis of the existing kinetic and thermodynamic data.[3] Even more recently there has appeared a communication[4] wherein the authors have trapped the hitherto elusive intermediate $\cdot\mathrm{N{=}N{-}R'}$.

We have studied the azo compounds **1–4** to prove a choice between the two equations. The synthesis of **1–4** was achieved by the mercuric oxide oxidation of the corresponding hydrazine, $\mathrm{RNHNHCH_2CH{=}CH_2}$, which was in turn obtained by the hydrolytic decarboxylation of *N*-alkyl-*N*′-allylbicarbamate.[5]

Thermolysis of **1** at 57 Torr and 131.6° produced methane (36%), 1-butene (33%), 1,5-hexadiene (19%), azomethane (4.6%), propene (0.7%), ethane (0.7%), and pentane (0.4%) based on the nitrogen formed at 30% completion. Nitric oxide[6] was found to suppress the radical chains, eliminate hydrocarbon formation, and decrease the thermolysis rate. The rate showed a slight increase upon further increasing the nitric oxide pressure. Experiments with ^{15}NO indicated that some of the nitrogen[7] was derived from the nitric oxide and that the rate constant was unchanged upon

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(1) H. Zollinger, "Azo and Diazo Chemistry, Aliphatic and Aromatic Compounds," Interscience, New York, N. Y., 1961, Chapter 12.

(2) C. Rüchardt, *Angew. Chem., Int. Ed. Engl.*, **9**, 830 (1970).

(3) S. W. Benson and H. E. O'Neal, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, **No.** 21, 31 (1970).

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(5) All new compounds gave satisfactory spectral and elemental analyses.

(6) The nitric oxide studies carried out here were modelled from the detailed study on azomethane of W. Forst and O. K. Rice, *Can. J. Chem.*, **41**, 562 (1963).

(7) Mass spectrometric analysis of the nitrogen produced from the runs of 1 with ^{15}NO at 126.35° for 90 min indicates that the ratio of $^{15}\mathrm{N}^{15}\mathrm{N}$ to $^{14}\mathrm{N}^{14}\mathrm{N}$ is less than 0.05 when the ^{15}NO to 1 ratio is less than 0.20. The formation of nitrogen from nitric oxide has been postulated by several workers as due to a reaction with nitrosoalkanes. See ref 6 and J. F Brown, Jr., *J. Amer. Chem. Soc.*, **79**, 2480 (1957); M. I. Christie, *Proc. Roy. Soc., Ser. A*, **249**, 248 (1958); B. G. Gowenlock and M. J. Healey, *J. Chem. Soc. B*, 1014 (1968).

Table I. Kinetic Parameters and Relative Rates at 122.3° for the Gas-Phase Thermolysis of the Azoalkanes **1–4** ($P_0 > 60$ Torr)

$RN{=}NCH_2CH{=}CH_2$		Inhibitor added	BDE[a] (R–H)	E_a, kcal mol^{-1}	Log A	10^5k, sec^{-1}	Rel rate
	R						
1	CH_3-	None	104 ± 1	35.4 + 0.7	14.51	0.794	
		^{15}NO		35.5 ± 0.7	14.36	0.407	0.138
2	n-C_3H_7-	^{15}NO	98 ± 2	35.6 ± 0.8	14.80	1.20	0.339
3	$(CH_3)_3C-$	^{15}NO	91 ± 1	29.8 ± 0.8	12.73	17.5	4.92
4	$CH_2{=}CHCH_2-$	None[b]	85 ± 1	36.1 ± 0.2[c]	15.54[c]	3.55	1.00

[a] Bond dissociation energy in kilocalories per mole for the R–H bond; see J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966). [b] Rate unchanged upon the addition of nitric oxide. [c] See ref 10.

correcting for the nitric oxide's contribution. Studies of **1** and **2** indicate that at low conversion (up to 5%) and at a nitric oxide–reactant ratio of 1:7–1:5, the total nitrogen formed can be used directly to calculate the rate constant, with very little loss of precision.[8]

The inhibited thermolysis of **3** produced approximately 15% of $^{15}N^{15}N$ and 30% of isobutene[9] based on $^{14}N^{14}N$. A correction was made for this in measuring the rate of nitrogen production from **3**. The kinetic parameters and relative rate constants obtained for **1–4**[10] are given in Table I.

How then can we decide between eq 1 and eq 2 from the set **1–4**? Ramsperger[11] has suggested, and Rüchardt[2] has supplied additional evidence for the criteria for eq 1, that the activation energy of the unsymmetrical compounds will be the mean of the activation energies for the corresponding two symmetrical compounds. Using known data for azomethane,[5,11,12] azopropane,[13] 2,2′-aziosobutane,[14] and 3,3′-azo-1-propene[10] we can predict rate constants at 122° for **1–3**.[15] If eq 2 is appropriate to the mechanism then we expect the first step to be rate determining and for the compounds **1–3** we would expect the allylic–nitrogen bond to be most readily cleaved. To a first approximation the thermolysis rates of these compounds should be one-half the rate of **4**. Steric effects are well documented to be of importance in the thermolysis of azo compounds[16] and may make the values different from one-half that of k_4. It seems unlikely that these effects would change the rate by more than one power of ten. If then eq 2 is representative of the true mechanism the rates of **1–3** will be in the range of 0.05–5 times that of **4**. The criteria for deciding between eq 1 and 2 are shown graphically in Figure 1.

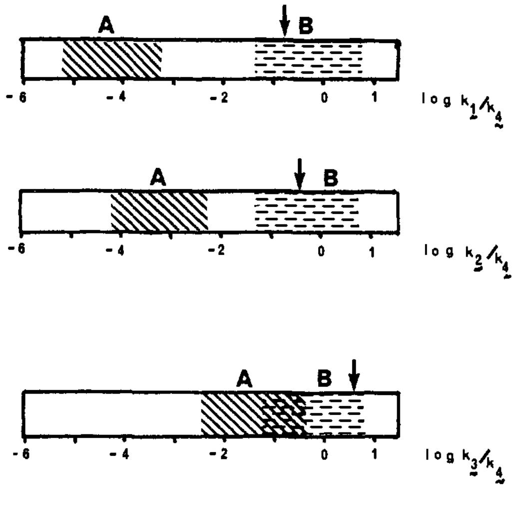

Figure 1. Graphical representation of the choice between eq 1 and eq 2.

It may be seen from Figure 1 that for all of the unsymmetrical azo compounds studied, **1**, **2**, and **3**, log k_n/k_4 falls in the region of eq 2. That the value of k_n/k_4 increases as the bulk of the R group increases is compatible with a steric effect.[16]

Secondary deuterium kinetic isotope effect studies of methylazo-3-propene-*1,1*-d_2 (**1**-d_2) provide further evidence in support of the two-fragment mechanism. Earlier we[10] observed in a study of secondary kinetic isoptope effects on **4** that if eq 1 is operative the value of $\Delta\Delta G^{\ddagger}$ is 60 cal mol^{-1} per deuterium, but if eq 2 is operative then the value of $\Delta\Delta G^{\ddagger}$ is 120 cal mol^{-1}. Examination of **1**-d_2 gives a k_H/k_D ratio of 1.28 ± 0.03 at 126.0° ($\Delta\Delta G^{\ddagger} = 98 \pm 9$ cal mol^{-1} per deuterium). This is comparable to the values generally encountered in the thermolysis of azo compounds wherein the transition state occurs late on the reaction coordinate.[2,16h,17] After the statistical correction of two is applied, the diallyl compound **4** is only 1.5 times faster than the *n*-propyl allyl compound **2** demonstrating that there is little, if any, effect on the rate upon changing the R–H bond dissociation energy by 13 kcal mol^{-1}. This coupled with the excellent Polanyi

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[8] The average of corrected rate constants obtained at 126.35° over the ^{15}NO:1 ratio range of 0.041–0.915 was found to be 8.13×10^{-6} sec^{-1} with a standard deviation of 0.44×10^{-6} sec^{-1}.

[9] The reaction of nitroso-*tert*-butane with ^{15}NO produced predominantly $^{14}N^{15}N$ and isobutene even at room temperature.

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[15] The rate constant for azomethane at 120° was obtained by using various sets of kinetic parameters[5,11,12] and taking their mean. The use of either the maximum or minimum extrapolated value does not alter the conclusion as the shaded area A in Figure 1 is shifted by only ±0.5 unit by such a choice.

[16] (a) C. G. Overberger and A. V. DiGiulio, *J. Amer. Chem. Soc.*, **81**, 2154 (1959); (b) C. G. Overberger, M. T. O'Shaughnessy, and H. Shalit, *ibid.*, 71, 2661 (1949); (c) C. G. Overberger and M. B. Berenbaum, *ibid.*, 73, 2618 (1951); (d) S. G. Cohen, S. J. Groszos, and D. B. Sparrow, *ibid.*, 72, 3947 (1950); (e) C. G. Overberger, W. H. Hale, M. B. Berenbaum, and A. B. Finestone, *ibid.*, 76, 6185 (1954); (f) C. G. Overberger, H. Biltech, A. B. Finestone, J. Litker, and J. Herbert, *ibid.*, 75, 2078 (1953); (g) J. Hinz and C. Rüchardt, *Tetrahedron Lett.*, 3095 (1970); (h) S. E. Scheppele and S. Seltzer, *J. Amer. Chem. Soc.*, **90** 358 (1968); (i) B. Strehlke, Ph.D. Thesis, University of Alberta, 1971; (j) D. J. Severn and E. M. Kosower, *J. Amer. Chem. Soc.*, **91**, 1710 (1969).

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plot observed by Al-Sader[10] for the symmetrical azoalkanes leads us to the conclusion that *in the gas phase, azo compounds fragment into two species in the rate-determining step.* This is best represented by eq 2 for azoalkanes, and is consistent with a similar conclusion obtained in the study of 1-pyrazolines.[18]

It is of particular interest to compare the activation energy obtained for **1**, **2**, and **4** with that of azoethane,[19] 48.5 kcal mol^{-1}. The decrease in activation energy, 12.4–13.0 kcal mol^{-1}, may be attributed to the allylic resonance energy affecting the rate-determining step. This is comparable to the generally accepted value.[20] Since the full significance of the allylic resonance energy is manifested, the transition state is like the initial cleavage products.

Acknowledgments. Financial assistance from the National Research Council of Canada and helpful discussions with Professor D. Darwish are gratefully acknowledged.

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Photochemical Redox Decomposition of Aqueous Azidopentaamminechromium(III)

Sir:

While photochemical substitution reactions of Cr(III) coordination compounds are quite common,[1,2] photochemical redox decompositions of Cr(III) complexes have not been observed before.[3] The results of the present investigation suggest that irradiation of aqueous $Cr(NH_3)_5N_3^{2+}$ at pH 1 in the charge-transfer (ligand to metal) band leads to redox decomposition of quantum yields 0.45 at 313 mμ and 0.4 at 263 mμ, whereas irradiation at longer wavelengths in the ligand-field bands leads to photoaquation yielding $Cr(NH_3)_4(H_2O)(N_3)^{2+}$.

Preliminary investigations as well as older observations[4] indicate that the Cr–N bond in $Cr(NH_3)_5N_3^{2+}$ is remarkably stable with regard to thermal substitution reactions. Contrary to other acidopentaamminechromium complexes, where, in thermal reactions preferentially the acido group is being substituted,[5] $Cr(NH_3)_5N_3^{2+}$ seems to show only ammonia aquation.

The photosensivity of $Cr(NH_3)_5N_3^{2+}$ was first reported by Linhard and Berthold.[4] Upon irradiation, they observed that the red color of an acidified solution of this complex turned to violet. This color change was accompanied by an increase of pH and formation of ammonium ions. Release of N_3^- was negligible.

We could confirm these observations if the wavelength of irradiation was restricted to the region of the ligand-field bands (maxima and extinction coefficients of the first two ligand-field bands: L_1 498 mμ, ϵ 144; L_2 382 mμ, ϵ 93).[6] The irradiated violet solution was treated with concentrated perchloric acid to precipitate an excess of the starting complex. The filtrate exhibited new absorption maxima at 515 and 393 mμ. Since only ammonia was released, we conclude that $Cr(NH_3)_4(H_2O)N_3^{2+}$ was formed in the photoreaction. It could not yet be decided whether $Cr(NH_3)_4(H_2O)N_3^{2+}$ was formed as the trans or cis isomer.

Irradiation of $Cr(NH_3)_5N_3^{2+}$ in 0.1 *M* $HClO_4$ at shorter wavelengths in the CTLM band (maximum at 263 mμ with ϵ 5000)[6] caused immediate evolution of nitrogen. Simultaneously, the red solution was bleaching and the pH was increasing. Ammonium was detected, but release of azide was negligible. Azide determinations were made by separation of N_3^- by an ion-exchange technique and formation of an Fe^{3+}–N_3 complex which was determined spectrophotometrically at 460 mμ, ϵ 3.68 × 10^3.[7] After continued irradiation, the solution of $Cr(NH_3)_5N_3^{2+}$ changed its color from red to a pale green. The photochemical reaction was followed spectrophotometrically. At all wavelengths, the optical density decreased except at the minimum at 435 mμ where a slight increase was observed. Two clear isosbestic points at 410 and 442 mμ exclude the formation of an intermediate species which could complicate the reaction by secondary photolysis. The decrease of the first ligand-field band at 498 mμ was proportional to the absorbed light intensity at least up to a reaction amount of 40%. Hence the photochemical reaction follows a first-order kinetics. After photolysis to completion, the pale green solution had a new maximum at 423 mμ with ϵ 64 per chromium.

Quantum yield determinations for disappearance of $Cr(NH_3)_5N_3^{2+}$ were made by measuring the decrease of optical density at the maximum of the first ligand-field band at 498 mμ, taking into account that the optical density at 498 mμ drops to a few per cent when the solution is photolyzed to completion. $K_3Fe(C_2O_4)_3$ actinometry was used.[8] At a 313-mμ irradiating wavelength (Osram high-pressure mercury lamp, 100 W; Schott filter No. 313), the quantum yield was 0.45; at 263 mμ (Hanovia xenon lamp, 150 W; Aminco monochromator), the quantum yield was 0.4. The volume of evolved nitrogen was measured and compared with the decrease of optical density at 498 mμ. Assuming that 1.5 mol of N_2 was formed per mole of chromium, about 90% of the required amount of nitrogen was recovered. These observations suggest that a redox decomposition occurs upon irradiation of $Cr(NH_3)_5N_3^{2+}$ in the CTLM band according to

$$Cr(NH_3)_5N_3^{2+} \longrightarrow Cr(NH_3)_5^{2+} + N_3$$

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