Table I. First-Order Rate Data for Solvolysis of Cyclopropylcarbinyl 3,5-Dinitrobenzoates in 60% Aqueous Acetone at 100°

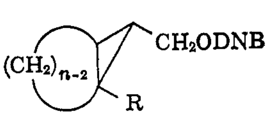
	Cyclopropylcarbinyl 3,5-dinitrobenzoate	k_1, sec^{-1}	Relative rates Obsd	Relative rates Calcd[a]	Lit.
1	Parent	4.30×10^{-7}	1.0	1.0	1.0
2	1-Methyl	2.13×10^{-6}	5.0	...	4.7[b,c] 4.8,[d] 5.5,[e] 50[f]
3	1′-Methyl	4.37×10^{-4}	1020	...	
4	*trans*-2-Methyl	4.75×10^{-6}	11.0	(11.0)	
5	*cis*-2-Methyl	3.50×10^{-6}	8.2	(8.2)	
6	2,2-Dimethyl	3.97×10^{-5}	92	90	96[b]
7	*trans,trans*-2,3-Dimethyl	5.33×10^{-5}	124	121	
8	*cis,cis*-2,3-Dimethyl	3.53×10^{-5}	82	67	
9	*cis,trans*-2,3-Dimethyl	3.45×10^{-5}	80	90	
10	*trans*-2,3,3-Trimethyl	2.12×10^{-4}	490	1000	
11	2,2,3,3-Tetramethyl	6.75×10^{-4}	1570	8100	
12	*trans*-2-Ethoxy	4.03×10^{-4}	940	...	
		Polycyclic Compounds			
13	X, $n = 8$	3.77×10^{-5}	88		
14	X, $n = 7$	2.20×10^{-5}	51		
15	X, $n = 6$	9.65×10^{-5}	220		
16	X, $n = 5$	1.70×10^{-5}	40		36[g]
17	XI	3.78×10^{-6}	8.8		
18	X, $n = 4$	...	...		1.3[h]
19	XII	4.00×10^{-4}	930		
20	XIII	5.42×10^{-4}	1260		
21	XIV	6.00×10^{-6}	14		
22	XV	4.43×10^{-5}	103		
23	XVI-PNB[7]	2.17×10^{-5} [7]			300[i]
24	XVII-PNB				1000[j]

[a] Calcd by eq 1. [b] Methanesulfonates in 96% ethanol at 20°.[6b] [c] Tosylates in acetic acid at 25°.[5a] [d] *p*-Methoxybenzenesulfonates in acetic acid at 25°.[5a] [e] Benzenesulfonates in acetic acid at 25°.[5a] [f] Chlorides in 50% ethanol. Rough comparison; rate constants were not reported at the same temperature. This ratio seems suspect. [g] Tosylates in acetic acid with added KOAc at 25°.[4a] Comparison made with data for the parent compound in acetic acid alone.[5a] [h] Tosylates in acetic acid at 17°.[4b] [i] Comparison assuming *p*-nitrobenzoates solvolyze six times slower than 3,5-dinitrobenzoates. [j] *p*-Nitrobenzoates in 90% acetone at 118.6°.[4c]

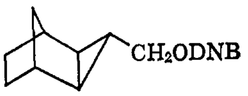
2- and 3-methyl substituents have a remarkably constant multiplicative effect. Each additional group enhances the rate independent of the number and location of its neighbors; the factor for a *trans*-2 or 3-methyl (11.0) is slightly larger than the *cis* factor (8.2) (eq 1).

$$k_{\text{subst}}/k_{\text{parent}} = 8.2^{N_{cis\text{-2 or 3-CH}_3}} \times 11.0^{N_{trans\text{-2 or 3-CH}_3}} \quad (1)$$

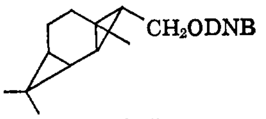
I–IX differ in their prediction of the extent of charge delocalization. Our methyl results are clearly most consistent with symmetrical structures VI–IX for the cyclopropylcarbinyl cation transition state and are not consistent with the bicyclobutonium formulations IV and V. An additional curious structural effect is easily explicable on this basis: the unexpected *decrease* in rate in the series 15 → 18, with an *increase* in ring strain. Structures VI–IX predict a *shortening* of the C-2,3 bond in the ion. A small, strained ring attached to these positions would experience an increase of strain during ionization. Perhaps the small deviations of the relative rates of **10** (twofold) and of **11** (fivefold) from their calculated values (Table I) can be attributed to the same effect. Compounds **23** and **24** are *accelerated* by an increase of strain of the second ring due to the opportunity for C-1,2 bond lengthening in the transition state.



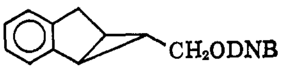
X, R = H
XII, R = CH$_3$



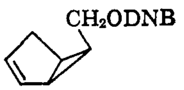
XI



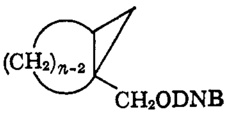
XIII



XIV



XV



XVI, $n = 5$
XVII, $n = 3$

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(20) A. P. Sloan Research Fellow, 1962–1966.
(21) American Machine and Foundry Fellow, 1963–1964.

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The Electronic Multiplicity of Thermally Generated Cyanonitrene. A Thermochemical "Heavy-Atom" Effect

Sir:

We have recently reported[1] that cyanonitrene (NCN) generated from thermal decomposition of cyanogen azide,[2] in the absence of a solvent, inserts[3] into the C–H

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(1) A. G. Anastassiou, H. E. Simmons, and F. D. Marsh, *J. Am. Chem. Soc.*, 87, 2296 (1965).

Table I. Stereochemistry of the Insertion of Cyanonitrene into the Tertiary C–H Bonds of *cis*- and *trans*-1,2-Dimethylcyclohexane as a Function of Solvent

Reaction	Solvent[a]	Hydrocarbon[b]	Temp, °C[c]	% *cis*-RNHCN[d] (2)	% *trans*-RNHCN[d] (3)	Over-all yield,[e] %
1[1]	None	*cis*	46.1	>98	<2	48
2	None	*cis*	43.5	>98	<2	43
3[1]	None	*trans*	46.1	<2	>98	48
4	None	*trans*	43.5	<2	>98	46
5	None	74% *cis*, 26% *trans*	43.5	83	17	52
6	CH_2Cl_2	*cis*	41.0	74	26	28
7	CH_2Cl_2	*trans*	41.0	34	66	35
8	CH_2Cl_2	74% *cis*, 26% *trans*	41.0	67	33	33
9	CH_2Br_2	*cis*	43.5	52	48	35
10	CH_2Br_2	*trans*	43.5	52	48	29
11	CH_2Br_2	74% *cis*, 26% *trans*	43.5	54	46	26

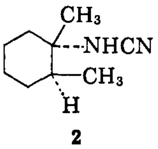
[a] A 10:1 solvent-to-hydrocarbon mixture was employed throughout. [b] In reactions 1–4, 6, 7, 9, and 10, the recovered hydrocarbon was analyzed gas chromatographically, and none of its isomer could be detected. [c] Maintained to within ±0.1° by means of a constant temperature bath. [d] Analyzed and identified as the corresponding amino and methylamino compounds according to the procedure indicated in ref 1. [e] Yield of a 1:1 mixture of amino- and methylamino-1,2-dimethylcyclohexanes, based on the sodium azide employed to prepare cyanogen azide.

bonds of saturated hydrocarbons to yield alkyl cyanamides (**1**) in an essentially stereospecific fashion. We

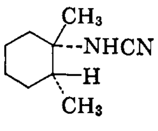
$$N_3CN \xrightarrow[-N_2]{\Delta} NCN \xrightarrow{RH} \underset{\mathbf{1}}{RNHCN}$$

have also indicated that the stereospecificity of the reaction, though favoring a one-step insertion by singlet NCN, does not eliminate the possibility of a two-step process involving hydrogen abstraction by triplet NCN followed by spin inversion and recombination of the resulting radical pair, provided this latter process occurs prior to inversion of the hydrocarbon radical.[4] We now wish to present definitive evidence in favor of the one-step process and to report a thermochemical "heavy-atom" effect observed during the course of this investigation.

If reactive NCN is in a singlet excited state, then its triplet ground state[5] should be accessible through collisional deactivation of the more energetic species with an inert solvent,[6] preferably one possessing a heavy atom.[7] Therefore we examined the stereochemical course of the insertion reaction employing the two isomeric 1,2-dimethylcyclohexanes as substrates and methylene chloride and methylene bromide as solvents.[8] The results are compiled in Table I.



2



3

The data tabulated clearly indicate that the stereospecificity of the reaction is lost, partially in CH_2Cl_2 and completely in CH_2Br_2. We interpret this to mean that NCN reacts partly as a triplet in CH_2Cl_2 and exclusively as a triplet in CH_2Br_2.[9] This is in complete agreement with the notion that triplet NCN is produced from collisional deactivation of singlet NCN, since CH_2Br_2, possessing a heavier halogen, is required to be the more effective of the two solvents in bringing about singlet–triplet interconversions.[7] The lower energy content of the NCN generated in CH_2Br_2 is further demonstrated by its greater affinity for tertiary C–H bonds to produce tertiary products. These average at 69% of the total mixture in CH_2Br_2 as compared to 51% in the neat hydrocarbon.

The poorer yields observed when the reaction was carried in a solvent do not in any way detract from our interpretation, since, even on the extreme assumption that the difference in yields is due exclusively to reaction of singlet NCN with solvent, one can readily estimate a minimum stereochemical crossover of 16% in CH_2Cl_2 and 26% in CH_2Br_2 as compared to <2% in the neat hydrocarbon.

On the basis of the data presented here, we conclude that *thermolysis of cyanogen azide proceeds with conservation of spin to yield singlet NCN which inserts stereospecifically into C–H bonds. This species can be*

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(2) F. D. Marsh and M. E. Hermes, *J. Am. Chem. Soc.*, **86**, 4506 (1964).

(3) The term insertion is used here to indicate end result rather than mechanistic detail.

(4) Inversion of the asymmetric center with respect to NHCN can occur either by rotation of the hydrocarbon radical by 180° prior to recombination with the counterradical, a process believed to be responsible for the loss of stereospecificity in additions of carbenes and nitrenes to *cis* and *trans* olefins, or by migration of NHCN to a site at which recombination would invert the configuration of the original hydrocarbon.

(5) The ground state of NCN is $^3\Sigma_g^-$: G. Herzberg and D. N. Travis, *Can. J. Phys.*, **42**, 1658 (1964); G. J. Pontrelli and A. G. Anastassiou, *J. Chem. Phys.*, **42**, 3735 (1965); E. Wasserman, L. Barash, and W. A. Yager, *J. Am. Chem. Soc.*, **87**, 2075 (1965); D. E. Milligan, M. E. Jacox, and A. M. Bass, *J. Chem. Phys.*, **43**, 3149 (1965).

(6) Reports of additions of collisionally deactivated fluorenylidene [M. Jones, Jr., and K. R. Rettig, *J. Am. Chem. Soc.*, **87**, 4013 (1965)], carbethoxynitrene [W. Lwowski and J. S. McConaghy, Jr., *ibid.*, **87**, 5490 (1965)], and dicyanocarbene [E. Ciganek, *ibid.*, **88**, 1979 (1966) to olefins, in the condensed phase, have appeared recently.

(7) Heavy atoms are known to enhance the probability of spin-forbidden transitions through coupling of spin and orbital angular momenta. See for example C. D. Dijkgraaf and G. J. Hoijtink, "Quantum Chemistry Symposium," *Tetrahedron Suppl.*, **2**, 179 (1963), and J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," John Wiley and Sons, Inc., New York, N. Y., 1963, pp 294–300.

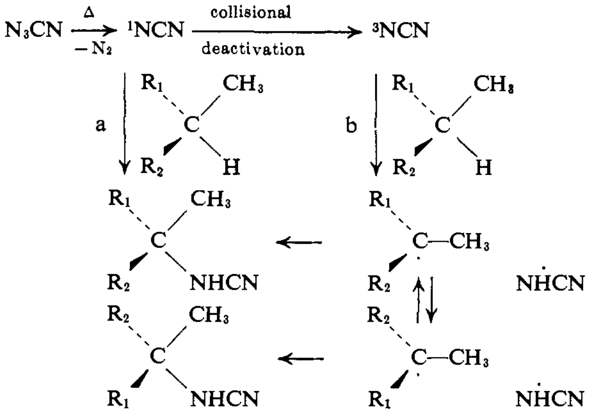
(8) At the temperatures employed here, CH_2Cl_2 and CH_2Br_2 do not react with NCN to any appreciable extent.

(9) The possibility that the same relative amounts of singlet and triplet NCN are present in the two solvents but in CH_2Cl_2, unlike CH_2Br_2, recombination occurs prior to complete equilibration of the stereoisomeric radical pairs appears unlikely in view of the similarity of the two halocarbons.

readily deactivated, through collisions with a suitable inert solvent, to triplet NCN which is incapable of stereospecific insertion[3] *into C–H bonds.* In the absence of a solvent, singlet NCN is in all probability the reactive species also in other reactions such as additions to aromatic[10] and olefinic[11] double bonds since these are in general less energetic processes than insertion.

The results reported here point to Scheme I in which path a is followed in the absence of a solvent, path b in methylene bromide, and a combination of a and b in methylene chloride.[12]

Scheme I



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(10) F. D. Marsh and H. E. Simons, *J. Am. Chem. Soc.*, **87**, 3529 (1965).

(11) A. G. Anastassiou, *ibid.*, **87**, 5512 (1965).

(12) Within the frame of this mechanism, equilibration between the stereoisomeric radicals is a rapid process compared with recombination.

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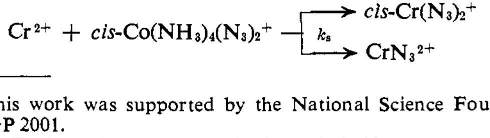
Received February 21, 1966

Parallel Single- and Double-Bridged Activated Complexes in Electron-Transfer Reactions[1]

Sir:

Although a double-bridged activated complex would appear to provide a reasonable path for an electron-transfer reaction,[2] such a path has been demonstrated only in the *cis*-$Cr(N_3)_2^+$–Cr^{2+} exchange reaction.[3] A search for a double-bridged activated complex has also been made in the *cis*-$Co(en)_2(OH_2)_2^{3+}$–Cr^{2+} and *cis*-CrF_2^+–Cr^{2+} systems,[4,5] but the experimental evidence indicates that transition states with a single bridging ligand are dominant in these cases.

In contrast with these results, we have found that the reaction of *cis*-$Co(NH_3)_4(N_3)_2^+$ (and of *cis*-$Co(en)_2(N_3)_2^+$) with chromium(II) proceeds *via* parallel single- and double-bridged activated complexes.



$$Cr^{2+} + cis\text{-}Co(NH_3)_4(N_3)_2^+ \begin{cases} \xrightarrow{k_d} cis\text{-}Cr(N_3)_2^+ \\ \xrightarrow{k_s} CrN_3^{2+} \end{cases} \quad (1)$$

Furthermore, we have demonstrated that, after the *cis*-$Cr(N_3)_2^+$–Cr^{2+} exchange which proceeds *via* the diazido-bridged transition state is substantially complete,[3] it is possible to detect the *cis*-$Cr(N_3)_2^+$–Cr^{2+} reaction that makes use of a single azide bridge.

When chromium(II) was added to an *excess* of *cis*-$Co(NH_3)_4(N_3)_2^+$, both CrN_3^{2+} and *cis*-$Cr(N_3)_2^+$ were produced.[6,7] The ratio [*cis*-$Cr(N_3)_2^+$]/[CrN_3^{2+}] was 0.6 ± 0.1 at 0° in 0.010 to 0.10 *M* perchloric acid. This ratio was found to be reasonably reproducible if the cobalt(III) complex was in excess. However, when an *excess* of chromium(II) was added to *cis*-$Co(NH_3)_4(N_3)_2^+$, the yield of *cis*-$Cr(N_3)_2^+$ appeared to be variable. In general the yield of *cis*-$Cr(N_3)_2^+$ was found to decrease with increasing [Cr^{2+}], and with increasing contact times between the excess chromium(II) and the *cis*-$Cr(N_3)_2^+$ produced in the *cis*-$Co(NH_3)_4(N_3)_2^+$–Cr^{2+} reaction. These results suggested chromium(II) catalysis of the aquation of *cis*-$Cr(N_3)_2^+$ *via* the single-bridged electron-transfer path[9]

$$cis\text{-}Cr(N_3)_2^+ + Cr^{2+} \longrightarrow [cis\text{-}N_3CrN_3Cr^{3+}]^* \longrightarrow CrN_3^{2+} + Cr^{2+} + N^{3-} \quad (2)$$

A direct test of reaction 2 was made by preparing *cis*-$Cr(N_3)_2^+$[10] and allowing it to react with chromium(II).

Table I. Kinetics of the Chromium(II)-Catalyzed Aquation of *cis*-$Cr(N_3)_2^+$ ([$HClO_4$] = 0.20 *M*, [*cis*-$Cr(N_3)_2^+$] = 3–4 × 10^{-5} *M*)[a]

15°		25°	
[Cr^{2+}], *M* × 10^3[b]	*k*, M^{-1} sec^{-1}	[Cr^{2+}], *M* × 10^3[b]	*k*, M^{-1} sec^{-1}
1.26	4.6	1.24	8.2
2.92	4.4	1.66	7.7
2.92	4.7	2.28	7.5
5.84	4.4	2.68	7.4
1.14	4.8[c]	2.87	7.6
2.32	4.4[c]	2.13	7.5[c]
2.58	4.4[c,d]	2.61	7.5[c]
Average	4.5	Average	7.6

[a] Except as noted, *cis*-$Cr(N_3)_2^+$ was prepared *in situ* by the *cis*-$Co(NH_3)_4(N_3)_2^+$–Cr^{2+} reaction. [b] Measured at the completion of the reaction from the increase in absorbance at 418 mμ upon reaction with oxygen. [c] *cis*-$Cr(N_3)_2^+$ prepared as indicated in footnote 10. [d] [$HClO_4$] = 0.080 *M*.

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(1) This work was supported by the National Science Foundation, Grant GP 2001.

(2) H. Taube, *Advan. Inorg. Radiochem.*, **1**, 1 (1959).

(3) R. Snellgrove and E. L. King, *J. Am. Chem. Soc.*, **84**, 4609 (1962).

(4) W. Kruse and H. Taube, *ibid.*, **82**, 526 (1960).

(5) Y. T. Chia and E. L. King, *Discussions Faraday Soc.*, **29**, 109 (1960).

(6) The separation of *cis*-$Cr(N_3)_2^+$ and CrN_3^{2+} was achieved by ion-exchange chromatography.[3] At the concentrations used, *both* complexes were adsorbed on the resin (Dowex 50X-8, 50–100 mesh). Elution with 0.2 and 1.5 *M* perchloric acid, followed by spectrophotometric measurements at 275 mμ (ε 5900) and 270 mμ (ε 3700), yielded the concentrations of *cis*-$Cr(N_3)_2^+$ and CrN_3^{2+}, respectively.

(7) Hydrazoic acid was also formed under these conditions. The amount of hydrazoic acid formed was estimated from the absorbance at 260 mμ in the fraction that passed directly through the column, and was found to be comparable to the CrN_3^{2+} formed. This observation indicates that the chromium(II)–hydrazoic acid reaction,[3,8] although rapid, does not compete with the faster chromium(II)–*cis*-$Co(NH_3)_4(N_3)_2^+$ reaction. Furthermore, although it is possible that electron transfer occurs first *to* the azide bridge, the production of hydrazoic acid demonstrates that the electron is ultimately transferred to the cobalt(III) center.

(8) M. Ardon and B. E. Mayer, *J. Chem. Soc.*, 2861 (1962).

(9) Chromium(II) and azide ion are shown as products of reaction 2. However, in the presence of excess chromium(II), hydrazoic acid is rapidly reduced.[3,8] The rate of this reaction was not measured. However, the following blank experiments were carried out to ascertain the effect of this reaction on the measurements presented in Table I. Hydrazoic acid in 0.20 *M* perchloric acid was generated *in situ* by the rapid reaction ($k > 10^3$ M^{-1} sec^{-1}) of chromium(II) (~2 × 10^{-3} *M*) with *trans*-$Co(NH_3)_4(N_3)_2^+$ (~3 × 10^{-5} *M*), and the absorbance at 275 mμ was measured as a function of time. No change in absorbance was observed after the mixing time of 10 sec, and we conclude that, under these conditions, any changes in absorbance due to the chromium(II)–hydrazoic acid reaction are too small to interfere with reaction 2. Furthermore, as expected, we conclude that *cis*-$Cr(N_3)_2^+$ is not formed in the *trans*-$Co(NH_3)_4(N_3)_2^+$–Cr^{2+} reaction.