

MECHANISTIC INVESTIGATIONS ON REACTIONS OF MOLECULAR NITROGEN  
WITH ORGANIC SPECIES

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**Abstract** - As shown in previous investigations, aryl cations can react with molecular nitrogen (dinitrogen) in solution, forming initially an ion-molecule pair which rearranges into an arenediazonium ion. Analogous experiments with precursors of carbenes suggest that "classical" carbenes react with N<sub>2</sub> only if no other substrate (solvent) is available. Carbene-type carbon atoms which are part of a (hetero-)aromatic ring system do however react slowly with N<sub>2</sub> even in solution.

Molecular orbital studies of the reactions of N<sub>2</sub> with these organic species are qualitatively compared with those of the known reactions of N<sub>2</sub> with transition metal complexes. The <sup>13</sup>C and <sup>15</sup>N NMR chemical shifts of diazoalkanes and diazonium ions correlate with the capability of these compounds to exchange their two nitrogens with external N<sub>2</sub> molecules.

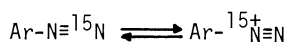
INTRODUCTION

Since the late 18th century it has been a paradigm that dinitrogen molecules are chemically almost inert - as seen in the German word "Stickstoff" (from "ersticken" = to suffocate) or French "azote" (from greek "αζωτικός" = azotos = without life, hostile to life; word proposed by A. Lavoisier 1787). Relatively few examples of reactivity have been observed since studies on this compound began. The leguminosae were known to "assimilate" N<sub>2</sub> and N<sub>2</sub> reacts (under rather drastic conditions!) with H<sub>2</sub> in the Haber-Bosch ammonia process. More recently, in 1965, Allen and Senoff (1) and soon afterwards Shilov et al. (2) found that certain metal-organic complexes are able to react with N<sub>2</sub>. With simple organic compounds, however, no reactions with N<sub>2</sub> were known except the N<sub>2</sub> exchange of diazomethane in N<sub>2</sub> matrixes, i.e. in the solid state (Ref. 3), and in the gas phase (Ref. 4).

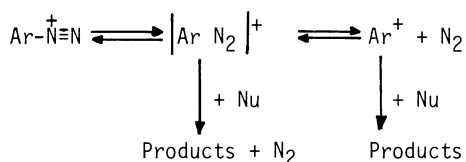
In contrast, N<sub>2</sub> as a leaving group from organic compounds is well known in dediazoniations of arene and alkane diazonium ions, of diazoalkanes and of azo compounds. In as early as 1940, Crossley et al. (5) postulated, on the basis of good kinetic and other evidence, a slow monomolecular and heterolytic dissociation of the C-N bond of arene diazonium ions into aryl cations and N<sub>2</sub>. An analogous, but fast dediazonation obviously takes place with alkane diazonium ions. The highly reactive cations formed in both cases were assumed to react very rapidly with nucleophiles (including solvent) in subsequent steps (recent review: Ref. 6).

E.S. Lewis et al. found in 1952 (7) that some of these reactions were not only first order with respect to diazonium ions, but also to nucleophiles. Lewis et al. (8) postulated a bimolecular process involving the attack of the nucleophile on the diazonium ion; Such a mechanism is, however, not supported by later evidence, e.g. substituent effects and kinetic isotope effects (Ref. 9).

In this situation we made the unconventional "anti-paradigmatic" proposal (Ref. 10) that the first step in arene diazonium ion dissociation is reversible. Experimental evidence for that hypothesis came first from the observation that the nitrogen in <sup>15</sup>N-labelled diazonium ions could exchange with unlabelled N<sub>2</sub> present in the solution and, second from the detection of an N<sub>α</sub>-N<sub>β</sub>-rearrangement in monolabelled arene diazonium ions:



The results of careful kinetic studies (Ref. 11) and of  $^{15}\text{N}$  experiments ( $\text{N}_\alpha\text{-N}_\beta$ -rearrangements and exchange with external  $\text{N}_2$ ), also secondary isotope effects with the 2,4,6- $\text{D}_3$ -benzene diazonium salt (Ref. 12), are consistent with the initial formation of an ion-molecule pair from which the free (solvated) aryl cation and  $\text{N}_2$  are formed. Both these intermediates can react with nucleophiles (Scheme 1).



Scheme 1

We think that this mechanism, in addition to being relevant to the dediazonation of arene diazonium ions, has a wider chemical interest for the back reaction:  $\text{Ar}^+ + \text{N}_2 \longrightarrow \text{Ar-N}_2^+$  is a process wherein a "simple" organic species reacts with dinitrogen in solution. That reaction is first of all interesting because it violates the paradigm of inertness of dinitrogen! We have put forward evidence for a "psychological barrier" to the acceptance of this contradiction (Ref. 13). In Th.S. Kuhn's nomenclature (14) this is a typical example for a "revolution" after a "scientific crisis", followed afterwards (e.g. in Ref. 11 and 12) by work which Kuhn calls "normal science", i.e. a period which is characterized by conventional and logical (i.e. Popperian) verification/falsification steps.

Two questions follow from that development:

- 1.) What is so specific about an aryl cation that it reacts with such an unconventional nucleophile as  $\text{N}_2$ ?
- 2.) Are there other highly reactive organic species which may react also with  $\text{N}_2$ ?

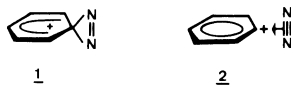
This paper is concerned with these two questions.

#### EXISTENCE OF ARYL CATIONS

With the possible exception of their involvement in a complex ring closure of an alkyne derivative studied by Hanack et al. (15), attempts to form aryl cations from sources other than arene diazonium ions have been unsuccessful (Ref. 16). Our group is also working on alternative substrates, but so far without success.

Molecular orbital studies dealing with the electronic structure of aryl cations have been made (Ref. 9, 17). The most sophisticated investigations are MINDO/3 and STO-3G MO calculations by Castenmiller and Buck (18) and Tasaka et al. (19). Castenmiller and Buck also investigated by MINDO/3 the energetics of the heterolytic dissociation of the benzene diazonium ion into a phenyl cation and dinitrogen and its back reaction. They found an energy difference of 205 kJ/mol (49.7 kcal/mol) between the benzene diazonium ion and the diazirinium ion **1**. The calculated energy barrier between the benzene diazonium ion and the phenyl cation +  $\text{N}_2$  was even larger, namely 356 kJ/mol (86.1 kcal/mol). In the reverse direction the activation energy for the reaction of the phenyl cation with  $\text{N}_2$  was found to be very low.

These results are not consistent with experimental data. Indeed the authors suspect that "the MINDO/3 potential energy surface for this system is incorrect for large internuclear distances".



It may be added here that our measurements of secondary isotope effects (12) in the dediazonium of 2,4,6-D<sub>3</sub>-benzene diazonium ion favour structure 2 relative to 1 for the postulated ion-molecule pair as intermediate.

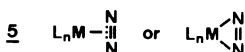
As it is known that the stability of diazonium ions is very different in the gas phase relative to a solution (Ref. 20), we suggested to M. Simonetta and his group that they apply their theoretical treatment to the benzene diazonium ion in presence of water molecules. This was done at the CNDO/2 level of approximation. The results (Ref. 21) demonstrate that the energy needed to separate the dinitrogen molecule from the phenyl residue is greatly reduced by solvation and that meta-stable intermediates are indeed predicted by CNDO/2. More detailed conclusions are however probably impossible.

In summary, the heterolytic mechanism involving an ion-molecule pair and the solvated phenyl cation as intermediates of heterolytic dediazonium is consistent with experimental data and cannot be refuted on the basis of MO theory in its present state of sophistication.

#### COMPARISON WITH DINITROGEN COMPLEXES OF ORGANOMETAL COMPOUNDS

It seems to be worthwhile to compare the back reaction of Scheme 1 with the addition of N<sub>2</sub> to transition metal complexes.

There are several types of dinitrogen metal complexes known:



Structures 3, 4 and more recently, 6 (Ref. 22) have been verified by X-ray crystallography and have been subjected to theoretical treatments (Ref. 23). To the best of our knowledge, however, there is no X-ray or neutron diffraction study to support structure 5. The "end-on" structure 3 may be comparable to arene diazonium ions, the "edge-on" (or "side-on" structure) 5 to our postulated ion-molecule pair 2 (or 1 respectively).

The bridging dinitrogen complexes 4 are not generally comparable with azoarenes or azoalkanes, as they are usually collinear. The NN bond length and the Raman active  $\nu$  N<sub>2</sub> are in some cases little different from those features of the free ligand. Sometimes, however, the NN distance increases up to 1.2 Å (with a respective fall of the Raman frequency) in spite of a retention of collinearity of the M-N=N-M' bonds.

In the end-on complexes (3) the NN bond is within 0.03 Å of that of the free ligand, but the MN distances are somewhat shorter than the value estimated for a single bond. The β-N becomes remarkably nucleophilic or, in other words, the electrophilicity of metal complexes is decreased by the addition of N<sub>2</sub>. Dinitrogen is both a weak σ-donor and a weak π-acid. dπ-pπ Back donation is considered to be important in stabilizing dinitrogen metal complexes. Similar qualitative comparisons can be made between the properties of the benzene diazonium ion and the phenyl cation e.g. the nucleophilicity/electrophilicity. In contrast to the dinitrogen metal complexes of type 3, the β-N of the benzene diazonium ion is not nucleophilic, but electrophilic. However the benzene diazonium ion is a very weak electrophile and, in particular, it is much less electrophilic than the phenyl cation. Adding N<sub>2</sub> to C<sub>6</sub>H<sub>5</sub><sup>+</sup> changes the electrophilicity of the phenyl cation in the same direction as addition of N<sub>2</sub> to L<sub>n</sub>M. There is therefore this similarity.

Unfortunately several claims for the detection of side-on mononuclear dinitrogen complexes of type 5 have not been substantiated by crystal structures. There are, however, many side-on complexes known with ethylene and acetylene ligands. This analogy, as well as the existence of side-on dinuclear dinitrogen complexes, does not falsify a priori our hypothesis of structure 2 for the ion-molecule pair in the dediazonium of arene diazonium ions.

In Figure 1, orbital representations for the end-on and for the side-on complexes of dinitrogen with metal complexes are given. In the first case the filled  $s$  orbital of  $N_2$  and in the second case the  $p\pi$  orbital of  $N_2$  overlaps with the vacant  $s$  orbital of the metal. In both cases, back donation from filled metal  $d\pi$  orbitals to vacant  $p\pi$  orbitals of  $N_2$  seems to be possible with respect to geometry and phase, demonstrating that the symmetry is correct for bonding. We shall come back to the type of bonding in these complexes in the next section of this paper.

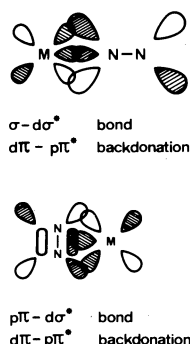


Figure 1

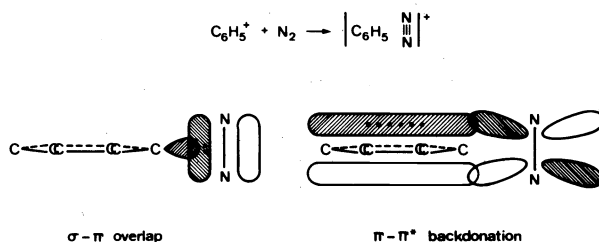


Figure 2

Figure 2 shows how  $\sigma^* - \pi$  overlap, as well as  $\pi - \pi^*$  back donation, may also be effective in the ion-molecule pair which we postulate.

#### OTHER POTENTIAL ORGANIC REAGENTS FOR DINITROGEN

We have discussed orbitals which may be effective in reactions of dinitrogen with metal complexes and with the phenyl cation. This comparison is, admittedly but probably inevitably, only qualitative and crude. It would also be useful to the discussion of this question if there was evidence for other highly reactive organic species binding to dinitrogen.

An interesting candidate may be a carbene. It is known that carbenes form cyclopropanes by reaction with alkenes. Skell and Woodward (24) postulated that singlet carbenes add to the olefin in a concerted reaction, whereas triplet carbenes cannot form cyclopropanes in one step, because it would be symmetry-forbidden. Singlet carbenes would therefore be expected to add stereospecifically and triplet carbenes non-stereospecifically. That conclusion was verified for the addition of *cis*-butene to fluorenylidene, formed by photolysis of diazo-fluorene (Ref. 25).

The stereospecificity of the singlet addition cannot however be due to a synchronous formation of two CC bonds. A direct attack of methylene on an olefin through a transition state with cyclopropane-like geometry is not symmetry-allowed as it contains 4 electrons, i.e. it is antiaromatic. The case for the addition of methylene to dinitrogen is the same (Figure 3).

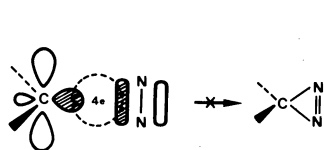


Figure 3

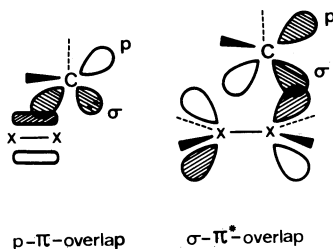


Figure 4

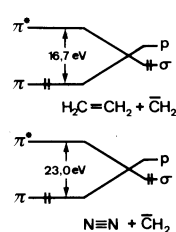



Figure 5

Calculations of R. Hoffmann and others (Ref. 26) suggest that the carbene and the olefin approach one another in such a way that  $p - \pi$  overlap becomes effective followed by  $\sigma - \pi^*$  overlap (Figure 4). In the first part of this concerted process the carbene is the electrophile. In the same step, however, the  $\sigma$ -HOMO of carbene overlaps with the  $\pi^*$ -LUMO of the olefin, the carbene is therefore nucleophilic for that part of the reaction.

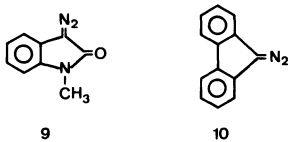
The correlation diagram for the simplest reaction of this type, namely  $\cdot CH_2 + H_2C=CH_2$ , can also be used for the reaction of methylene with dinitrogen (see Figure 5). It is calculated that the latter reaction, which leads to the aziridine, is significantly less favourable energetically than the former.

A more detailed theoretical study on the bonding nature of dinitrogen with methylene and with transition metal complexes has been made recently by Yamabe, Fukui and coworkers (27). They compared orbital interactions in end-on  $N_2$ -metal complexes 3, side-on mononuclear  $N_2$ -metal complexes 5, diazomethane ( $CH_2=N=N$ ; 7) and diazirine ( $CH_2$  ; 8). Their calculations show that for the bonding energy not only the energy gap between HOMO's and LUMO's, but also the geometry, i.e. the degree of overlapping of the MO's, is decisive.

The calculations of Yamabe and Fukui indicate that in diazomethane (7)  $\sigma$  donation is more important to the formation of the C-N bond than  $\pi$  back donation; the weakening of the NN bond is due only to  $\pi$  back donation. In the diazirine (8) however NN bond weakening is due to  $\pi$  back donation plus charge transfer interaction from  $\pi$  orbitals of  $N_2$  to  $n_C$  of  $CH_2$ . For the  $N_2$ -metal complexes,  $\sigma$  donation is the more important factor for the formation of the MN bond than  $\pi$  back donation. The NN bond of the side-on complex (5) is considerably weakened in comparison with that of the end-on complex (3). The total stabilization energies due to complex formation are 13.66 and 13.16 eV for the end-on and the side-on complexes, respectively. Therefore, the end-on complex is more stable, but not so much more that the formation of side-on complexes would look very unrealistic.

As experimental physical organic chemists, we decided to search for evidence of reactions between carbenes and nitrogen. As in our previous work with arene-diazonium ions, high concentrations of nitrogen, entailing the use of a pressurized system, were considered desirable. This limited us to generating our carbenes in thermally induced reactions. There are many examples of photochemically induced formations of carbenes, but initial studies pointed to the decomposition of a diazoalkane or a diazoketone as the only basic route.

We choose 1-methyl-3-diazoindole (9) and 9-diazoindole (10) because their thermal dediazonation is fairly well investigated with respect to products and because these precursors showed rates of reactivity which might allow nitrogen exchange to be detected.



Both compounds were labelled with  $^{15}N$  and the thermolyses were run at 300 to 1000 atm. in an autoclave. The original investigators of the thermolysis of 9 (Ref. 28) used ethanol as solvent; we changed it to hexafluoroisopropanol because our previous work (Ref. 10) showed that the solubility of dinitrogen is much larger in that solvent. The reactions were stopped after 50 to 80% of the diazo compound had decomposed. The residual diazo compound was analyzed for a potential decrease in  $^{15}N$  content in a mass spectrometer, either directly or after forming the hydrazone by borohydride reduction.

The decomposition of 1-methyl-3-diazoindole is extremely sensitive to impurities and to the reaction vessels used in the autoclave. This probably accounts for our observation in a series of dinitrogen exchange experiments with  $^{15}N$ -labelled 1-methyl-3-diazoindole at 800 and 1000 atm. of  $^{14}N_2$  pressure. The rate of dediazonation decreased in that series by a factor of 10. The determination of  $^{15}N$  in the residual diazo compound after 39 to 54% reaction showed very little nitrogen exchange (0.3%) at the first experiment but in the later experiments, we found a 1.26 to 2.68% exchange of diazo- $^{15}N$  with external dinitrogen at 800 to 1000 atm.  $N_2$  pressure, respectively. Using always the same equipment, however, the overall rate of dediazonation decreased again and no exchange of nitrogen was observed (note a).

We interpret these results as evidence for a reaction of the carbene with dinitrogen, but also as evidence that this reaction can be suppressed easily by apparently small changes in the reaction system. We found that the decomposition of 1-methyl-3-diazoindole on the material was dependent on the reaction vessel. The series of pressure experiments reported above was made in a Teflon-coated autoclave. It seems likely that in that series a change in the surface properties or chemical composition of the Teflon was responsible for the observed changes in rate and in nitrogen exchange.

We conclude from these results that there are at least two competitive reaction pathways for the decomposition of 1-methyl-3-diazoindole, one of which gives an intermediate that can react with external dinitrogen to regenerate the starting material. However, that is a reaction which takes place to a much smaller extent than the corresponding back reaction of

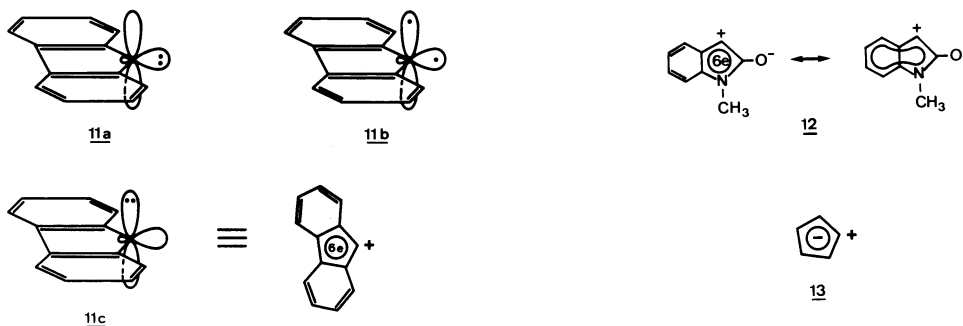
Note a: Details of these experiments will be published in a later paper.

the dediazonation of the benzene diazonium ion.

The thermolysis of 9-diazo fluorene (10) has been studied (Ref. 29). We investigated the possibility of an exchange of the  $^{15}\text{N}$ -labelled diazo group of 10 accompanying the thermal decomposition, using pure fluorinated inert solvent mixtures under 500-1000 atm. of unlabelled molecular nitrogen. The solvents were chosen for their inertness towards carbenes and their excellence as solvents for nitrogen gas, but in spite of this no exchange with external dinitrogen could be observed.

## DISCUSSION

It is well known that carbenes react either as singlets or as triplets. Singlet carbenes may have either nucleophilic or electrophilic reactivity. In the case of the carbenes formed from (9) and (10) the electrophilic character of the singlet is increased by aromatization of the 5-membered rings. For fluorylidene (11), a mesomeric formula 11c with an empty  $sp^2$  orbital on the carbene carbon has to be taken into account in addition to the conventional formulae for the singlet (11a) and the triplet (11b).



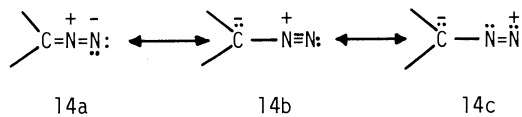
The analogous singlet carbene from 1-methyl-3-diazo oxindole is represented by 12.

Structures 11c and 12 are electronically comparable to the arene cations derived (formally) by hydride abstraction from phenanthrene at the 9-position and from the anion of 2-hydroxy-indole at the 3-position. Indole is considered here as an aromatic analogue of naphthalene. Furthermore we note that the aromaticity of the two six-membered rings of naphthalene is only slightly lower than that of benzene, whereas the reactivity and the physical parameters of anthracene and phenanthrene indicate clearly that the six-membered rings in the centers of those molecules have less aromatic character than the other two rings as demonstrated by Diels-Alder reactions of the middle ring of anthracene and by addition reactions at the 9,10-double bond of phenanthrene.

On the basis of these analogies one expects that the carbene 12 will bear a greater resemblance to a phenyl cation than fluorylidene (11). This conclusion is consistent with our finding that a small amount of dinitrogen exchange occurs between 1-methyl-3-diazo oxindole (9) and external  $\text{N}_2$  whereas no exchange is detected in the case of 9-diazo fluorene. An empty  $sp^2$  orbital at the carbene carbon atom due to the incorporation of that atom in a ring of relatively high aromaticity seems to be a condition for a reaction with dinitrogen.

On the basis of these conclusions one expects that the reactivity of cyclopentadienylidene (13) with dinitrogen should be still higher.






There is an interesting correlation with NMR spectra of diazo and diazonium compounds. Roberts et al. (Ref. 30) compared  $^{15}\text{N}$ - and  $^{13}\text{C}$ -NMR spectra of a large number of diazoalkanes and arenediazonium compounds which would be expected to possess different degrees of ability to stabilize structures of the type 14b and/or 14c relative to 14a:



Some of their results are summarized in Table 1.

Table 1

$^{13}\text{C}$  and  $^{15}\text{N}$  NMR Chemical Shifts of Diazomethyl Carbons and Nitrogen of Diazo and Diazonium Compounds, after Roberts et al. (Ref. 30)

Compound	$\delta^{13}\text{C}$	$\delta^{15}\text{N}_1$
$\text{H}_2\text{C}=\text{N}_2$	23.3	90
	47.2	76.8
	63.2	89.0
	67.1	95.8
	x = H 72.2 x = CN 92.6	106.2 147.1
	x = O <sup>-</sup> 79.8 x = OH 102.1 x = H 115.8 x = NO <sub>2</sub> 123.0	117.1 146.8 150.2 152.2

It is evident from the series of diazoalkanes in Table 1 that starting with diazomethane and ending with 2,3,4,5-tetracyano-1-diazocyclopentadiene the dipolar character of these compounds increases and approaches structures with a full diazonio group ( $-\overset{+}{\text{N}}\equiv\text{N}$ ).

We have therefore begun to investigate nitrogen exchange reactions of 2,3,4,5-tetracyano-1-diazocyclopentadiene and related compounds. From these studies we hope to gain support for our hypothesis relating to the reactions of dinitrogen molecules with organic species in solution.

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