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THE CAPACITY OF AN α-NITROALKYL RADICAL FOR HYDROGEN ABSTRACTION

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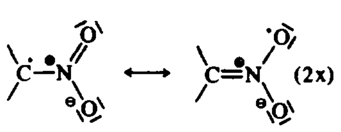
Abstract—Photochemical decomposition of 2-iodo-2-nitroadamantane in several hydrogen donating solvents, gives rise to formation of α-nitroalkyl radicals. Such ambident radicals can abstract hydrogen from the solvent via oxygen, resulting in a nitronic acid which decomposes exclusively into adamantanone. Alternately the abstraction can take place via carbon to give 2-nitroadamantane. The product distribution is strongly influenced by electron-withdrawing substituents in the hydrogen donor. The oxidation products derived from the solvent have been detected. All the experiments point towards a minor stabilisation of a carbon radical by a nitro group. INDO-calculations on the nitromethyl radical are in good agreement with this lack of stabilization.

INTRODUCTION

The α-nitroalkyl radical 1 plays a dominant role in various reactions, such as the oxidation of nitronate anions to ketones by oxygen[1] and to *vic*-dinitroalkanes by metal ions.[2] Russell and Kornblum[3] proved that the substitution of chloride in *p*-nitrobenzyl chloride by 2-nitropropanate anion proceeds via the 2-nitropropyl radical. Engberts *et al.* have shown that sulfinate elimination from α-sulfonyl-nitroalkane radical anions leads to α-nitroalkyl radicals.[4] In an earlier study we found[5] that α-nitroalkyl radicals are also formed as intermediates in the complicated photolysis of α-nitroso-nitroalkanes. In all these processes the fate of the α-nitroalkyl radical varies strongly with the nature of the reaction.

In order to study unimolecular reactions of the α-nitroalkyl radical or a typical radical reaction such as hydrogen abstraction, we needed a cleaner method for the generation of the α-nitroalkyl radical. The present study shows that photolysis of α-iodo-nitroalkanes meets this requirement.

The ambident character of the α-nitroalkyl radical. In the α-nitroalkyl radical the unpaired electron can formally be localized on carbon or on oxygen (2). It is generally accepted that delocalisation will lead to stabilization of the radical with respect to either canonical structure.



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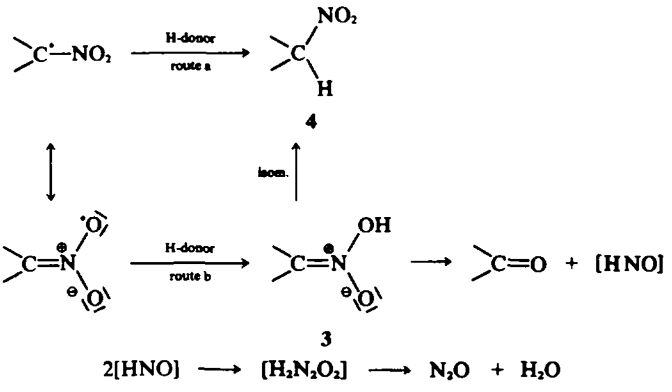
A priori hydrogen abstraction by such a radical can be accomplished in two ways (Scheme 1), viz. (a) via its O atom leading to the corresponding *aci*-nitro derivative 3 (a nitronic acid) and (b) via the C atom resulting in the nitroalkane 4.

In this connection it is important to note that simple aliphatic nitronic acids are not stable and give rise to several decomposition reactions.[6] Most important is the decomposition to ketones and dinitrogen oxide (N_2O). When catalysed by mineral acids this is known as the



Scheme 1. Mechanism of the photolysis of 2-iodo-2-nitroadamantane 5 in a hydrogen donating solvent.

Nef-reaction. Alternatively isomerization to the thermodynamically more stable nitro derivative may occur. Both possibilities are outlined in Scheme 1. It is the purpose of this investigation to find out which of these routes takes place with preference.

RESULTS

Photolysis of 2-iodo-2-nitroadamantane in hydrogen donating solvents. The solution phase photochemical behaviour of iodoalkanes has attracted relatively little attention in literature.[7-9] Commonly HI-elimination is an important process which gives rise to formation of olefins. In order to avoid this we have chosen the photolysis of 2-iodo-2-nitroadamantane **5** as a convenient route to an α-nitroalkyl radical, that does not easily lose hydrogen.

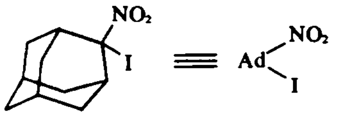


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Table 1. Product yields from photolysis of 2-iodo-2-nitroadamantane **5** in hydrogen donating solvents. Yields in % of **5**[a])

solvent (C-H bond energy) b)	Ad=O	$\mathrm{Ad}\genfrac{}{}{0pt}{}{\mathrm{NO_2}}{\mathrm{H}}$
cumene (70)	91	-
ethylbenzene (74)	81	5
4-chloro-ethylbenzene	19	60
3-chloro-ethylbenzene	25	62
4-cyano-ethylbenzene	10	51 c)
cyclopentene (~ 77)	60	15
isopropyl alcohol (84)	45	33
isopropyl alcohol-o-d	41	34 d)
cyclopentene/MeOD (4:1)	60	15 d)

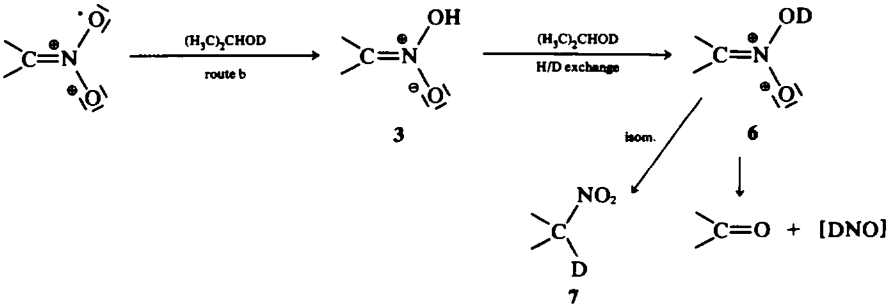
a)Initial conc. 0·235 M.
b)In kcal/mole, according to lit.[12].
c)Unidentified products also present.
d)No deuterium incorporation was found.

Homolysis of the C–I bond is generally assumed to be the primary process, although a recent publication[10] reports the *hetero*lytic removal of the iodide ion as an important route. In our system this path is highly unfavourable as a consequence of the strongly electron-withdrawing α-nitro group, destabilizing a hypothetical α-nitrocarbenium ion.

Upon photolysis of 2-iodo-2-nitroadamantane in isopropyl alcohol, the following products are formed: adamantanone (45%), 2-nitro-adamantane (33%), acetone (50%), iodine (65%), dinitrogen oxide (7%) and water (Table 1). Thus hydrogen abstraction can be accomplished by the α-nitroalkyl radical, judging from the formation of nitroadamantane and the dehydrogenation of the solvent to acetone.

In principle 2-nitroadamantane can be formed via two routes (Scheme 1). To distinguish between these routes we carried out a photolysis of 2-iodo-2-nitroadamantane **5** in O-deuterated isopropyl alcohol. Abstraction of the carbon-linked hydrogen from this solvent by the α-nitroadamantyl radical via its α-carbon atom (route a) gives rise to α-hydrogen substituted 2-nitroadamantane. On the other hand, by abstraction via one of its O atoms (route b), nitronic acid **3** (initially O–H) is formed, which gives a rapid deuterium exchange resulting in a nitronic acid O-d **6**. The latter should give α-deuterated 2-nitroadamantane **7**.

In fact mass spectrometrical analysis shows that no deuterium incorporation in 2-nitroadamantane takes place. It may thus be concluded that nitroalkane formation does not occur via isomerisation of the nitronic acid but that 2-nitroadamantane is produced exclusively by hydrogen abstraction via carbon. Consequently the yield of 2-nitroadamantane is a direct measure for the importance of the corresponding route a. Because 2-nitroadamantane cannot be transformed to adamantanone under the reaction conditions, the latter must arise exclusively via route b by decomposition of nitronic acid. The adamantanone yield of 45% and the nitroadamantane yield of 33% indicates that the nitroadamantyl radical abstracts hydrogen from *isopropyl alcohol* more efficiently via oxygen (route b) than via carbon (route a). Apparently the nitronic acid does not even partially isomerise to the nitro compound, but it decomposes far more rapidly. This conclusion is also supported by our observation that the decomposition of *aci*-nitrocyclododecane (a relatively stable compound) in both methanol and methylene chloride gives almost exclusively



rise to cyclododecanone (80%), in addition to nitrocyclododecane (~6%) and minor amounts of cyclododecanone-oxime and cyclododecanol.

When ethylbenzene is used as hydrogen donor instead of isopropyl alcohol, adamantanone (81%) and 2-nitroadamantane (5%) are formed upon photolysis of **5**. No molecular iodine was found because the α-phenylethyl radical resulting after H-abstraction from ethylbenzene can be trapped by iodine and this leads ultimately to photochemically stable ring substituted products, e.g. 4-ethyl-iodobenzene (48%) and 2-ethyl-iodobenzene (32%). (No α-iodoethylbenzene is formed due to its photochemical instability). The total yield of products derived from the solvent almost equals the yield of adamantane derivatives; the deuterium exchange experiment described above shows that 2-nitroadamantane is not formed by abstraction via oxygen. Thus the yield of adamantanone is a direct measure of the degree of hydrogen abstraction via oxygen.

The (unimolecular) decompostion of the α-nitroalkyl radical into NO and ketone, as described in the subsequent article,[11] is unimportant in hydrogen donating solvents. Product distribution in several hydrogen donating solvents are summarized in Table 1. As can be seen, the product distribution is strongly influenced by the solvent. Comparing the product distribution with bond dissociation energies (of the weakest C–H bond in each H-donor) of the solvent series cumene, ethylbenzene, cyclopentene and isopropyl alcohol, it is obvious that the ratio of hydrogen abstraction via oxygen or via carbon (in the α-nitroalkyl radical), decreases with increasing bond dissociation energy.

DISCUSSION

Polar contributions in the transition state of hydrogen abstractions are well documented.[13] These are described as follows:

$$R{-}H + {}^{\cdot}X \rightarrow [R^{\cdot}H^{\cdot}X^{\cdot} \leftrightarrow R^{\oplus}H^{\cdot}X^{\ominus}] \rightarrow R^{\cdot} + H{-}X.$$

The expected selectivity based on (C–H) bond dissociation energies can be reversed in the case of radicals $X^{\cdot}$ with high electron affinity, like for instance chlorine. Upon substituting the hydrogen-donor RH with electron-withdrawing groups the polar contribution involving $R^{\oplus}$ is naturally destabilized and when X = α-nitroalkyl, abstraction proceeds via the position with highest unpaired electron density. In the case that the polar contribution is important, abstraction occurs via oxygen as is expected from the charge distribution in the α-nitroalkyl radical.

In order to determine the unpaired electron distribution as well as the total charge distribution in the α-nitroalkyl radical, we performed MO-calculations with the INDO-approximation on the nitromethyl radical according to Pople and Beveridge.[14] Coordinates of the positions of the nuclei are derived from a series of nitro compounds in which the nitro group is attached to a π-system. The radical is supposed to have planar geometry with: C–H = 1·09 Å, C–N = 1·39 Å, N–O = 1·22 Å, H–C–H angle = 112° and O–N–O angle = 123°. The C–N bond length is varied in steps of 0·06 Å to a minimum total energy of −54·5427029 a.u. The total unpaired electron density (spin density) of the nitromethyl radical is given below.

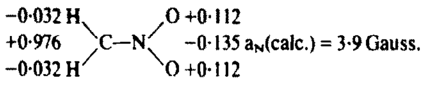


Fig. 1. Calculated total spin density distribution on the nitromethyl radical.

The spin density at the C atom is very close to 1 thus indicating that a nitro group is hardly capable of interacting with a radical centre on carbon in α-position, and thus no stabilising influence can be exerted. The unpaired electron density on C_α in the adamantyl system as we have studied it, will be lower than the calculated value in Fig. 1 due to the stabilising "alkyl" groups attached to the α-C atom, instead of the two hydrogens in the model used in the calculation. The calculated hfs coupling constants are in good agreement with the experimental data obtained by Chachaty and Rosilio[15a] (a_N = 6 Gauss) and Russell[15b] (a_N = 4 Gauss).

The total charge distribution is outlined below and reveals that the majority of the negative charge is located on both oxygen atoms of the nitro group.

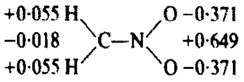


Fig. 2. Calculated total charge density distribution on the nitromethyl radical.

The varying adamantanone/nitroadamantane ratio for several hydrogen donors as given in Table 1 may be qualitatively understood from these INDO data using a perturbational treatment analogous to the one applied by Hudson and Klopman[16] to closed shell systems.

The adamantanone can be considered as the "charge controlled" product and 2-nitroadamantane as the "orbital controlled" product (cf. electron densities). Obviously, the hydrogen abstraction by the α-nitroalkyl radical is a highly "charge controlled" process, which is in contrast to radical reactions in general. Upon substitution of the hydrogen donor by electron-withdrawing groups (Table 1) the attack of the strongly electron deficient oxygen (from the α-nitroalkyl radical) on the H-donor becomes less favourable, thus logically explaining the increasing yield of the nitroalkane.

As far as we know this is the first example of the application of the perturbation theory to an ambident radical.

EXPERIMENTAL

M.ps are uncorrected. NMR spectra were determined on a Varian A-60 instrument, using TMS as internal standard. IR spectra were recorded on a Perkin Elmer 257 or a Unicam SP200, UV spectra on a Zeiss PMQ II. Mass spectra were recorded on a

AEI MS-902 mass spectrometer. The INDO calculation program was adapted to a CDC-computer at the University of Groningen, Prof. M. J. Janssen, Laboratory for Organic Chemistry, The Netherlands.

Starting materials. 2-Iodo-2-nitroadamantane was prepared by the procedure of Kornblum,[17] which is based on the electrophilic attack of iodine on the *aci*-form of an aliphatic nitro compound in aqueous soln at 0°. As soon as the product was formed it was extracted in a floating ether-layer to shift the equilibrium to the product-side. The organic layer was rapidly washed with a dil. $Na_2S_2O_3$ aq. This procedure resulted in analytically pure material, yield 70% faint yellow crystals, m.p. = 126–127° IR ($CHCl_3$): 1538 and 1340 cm^{-1}; UV (CH_2Cl_2): $\lambda_{max} = 308$ nm, $\epsilon_{max} = 690$; NMR ($CDCl_3$): $\delta = 1{\cdot}85$ ppm (m, 8H), $\delta = 2{\cdot}25$ ppm (m, 4H), $\delta = 2{\cdot}88$ ppm (m, 2H). 2-Nitroadamantane was prepared by trifluoroperacetic acid oxidation of the corresponding oxime.[18] 4-Chloro-ethylbenzene,[19] 3-chloro-ethylbenzene[20] and 4-cyano-ethylbenzene[21] were synthezised according to literature procedures. *Aci*-nitrocyclododecane was prepared by carefully acidifying (towards Congo Red[22]) an alkaline soln of nitrocyclododecane.[18]

Photolysis. The photolyses were carried out in a Pyrex glass vessel (transmission at 300 nm about 35%) fitted with a cooling jacket. A Philips superhigh pressure mercury arc SP500W was used. Dry Helium gas was passed through the soln (mostly 0·06 M) during the photolysis. The temp. was −10°. All irradiations extended over 5 hr when no iodine formation could be detected (viz. in cumene and ethylbenzenes) and 18 hr when the production of iodine reduced the reaction rate (in isopropyl alcohol). The thermal decomposition at this temp. is negligible. Iodine was determined by its visible absorption at 505 nm. The quantitative data were determined by GLC on a 3 m 20% silicone oil SE30 ($\phi = 8$ mm) on 80/100 Chromosorb AW column and adamantane as internal standard. Both acetone in isopropyl alcohol and N_2O were quantitatively determined on a 3 m 25% Carbowax 20 M ($\phi = 8$ mm) on 80/100 Chromosorb AW stainless steel column with 3-pentanone as the standard. The deuterium content of 2-nitroadamantane may easily be checked by mass spectrometric analysis of the $m/e = 135$ (parent $-NO_2$) peak. No deuterium was incorporated in a blanc experiment of 2-nitroadamantane in isopropyl alcohol-O-d.

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