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PHOTOCHEMISTRY OF N_2O_5 WITH ADAMANTANES

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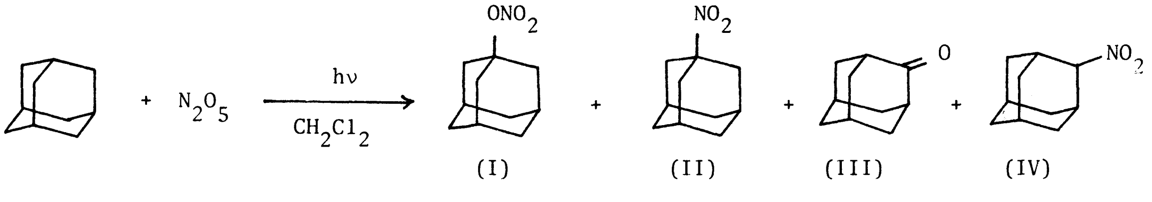
Photochemical reaction of N_2O_5 with adamantane is investigated. Products were 1-adamantyl nitrate(1), 1-nitroadamantane(II), adamantanone(III), and 2-nitroadamantane(IV), in the ratio of 5.5 : 4.4 : 2.2 : 1. The reaction is shown to proceed via triplet state of N_2O_5 and to have a typical chain character from the quantum yield measurement. $NO_3\cdot$ is shown to be a chain carrier.

In the course of radical substitution reaction of adamantanes, relative reactivity ratios (intramolecular ratio, bridgehead to bridge and/or intermolecular ratio, substituted to unsubstituted) are shown to be convenient "reaction parameters" to elucidate the reaction mechanism[1-3]. Thus adamantane becomes one of the most convenient model system. Now we wish to report the free radical substitution of adamantane with N_2O_5 under irradiation, especially focused on the reactivity of radicals formed on excitation of N_2O_5.

Irradiation of methylene chloride (100ml) solution of adamantane (5g) and N_2O_5 (5g) with 100 w high-pressure mercury lamp in pyrex vessel at 0°, gave four products. These were 1-adamantyl nitrate(I), 1-nitroadamantane(II), adamantanone(III), and 2-nitroadamantane(IV) in the ratio of 5.5 : 4.4 : 2.2 : 1[4]. (Scheme I). The yield of products was practically quantitative based on consumed adamantane.



Scheme I

N_2O_5 had an absorption at ca. 275 nm with tail up to 310 nm in methylene chloride. In acetonitrile, λ_{max} of the shoulder shifted by ca. 10 nm to shorter wavelength. This result suggests that the first excited state of N_2O_5 is (n π*). On irradiation of the solution of N_2O_5 and adamantane with light of longer wave length (λ>315 nm), no reaction took place. However, addition of benzophenone (E_t=68.5 kcal/mol) to the solution resulted in the sensitization of the products. Benzil (E_t=55 kcal/mol) was inefficient as a sensitizer of the reaction under the same condition. These facts suggest that the present reaction proceeds via (n π*) triplet state of N_2O_5 which is formed by intersystem crossing of singlet N_2O_5 (formed by irradiation with λ<315nm). This assumption is also supported by the quenching effect of oxygen on the reaction. Quantum yields were measured according to the standard method[5] utilizing pottassium ferrioxalate actinometer[6] and found to be 18.7 for the disappearance of adamantane and 8.0 for the formation of I. These values show that the reaction has a typical chain character. Plausible mechanism is shown in Scheme II. A chain carrier of the reaction must be $NO_3\cdot$ because NO_2 does not react with cyclohexane at room temperature[7], and besides does not cause chain reaction with isobutane on excitation, where maximum quantum yield of the formation of t-nitrobutane was reported to be only 0.35[8], much smaller than the quantum yield of the present reaction. Therefore the contribution of the reaction (3) is concluded not important.

Thus, in most part, adamantyl radical which is formed via hydrogen abstraction by $NO_3\cdot$ does not seem to react with NO_2 to give products, as postulated in the thermal reaction of N_2O_5 with cyclohexane[7], but seems to attack N_2O_5 to reproduce the chain carrier (reaction (5), (6), (8), and (9)). Since N_2O_5 was shown to convert cyclohexyl nitrite to nitrate[7], the reaction (10) is reasonably suggested.

Scheme II Plausible Mechanism for the Reaction

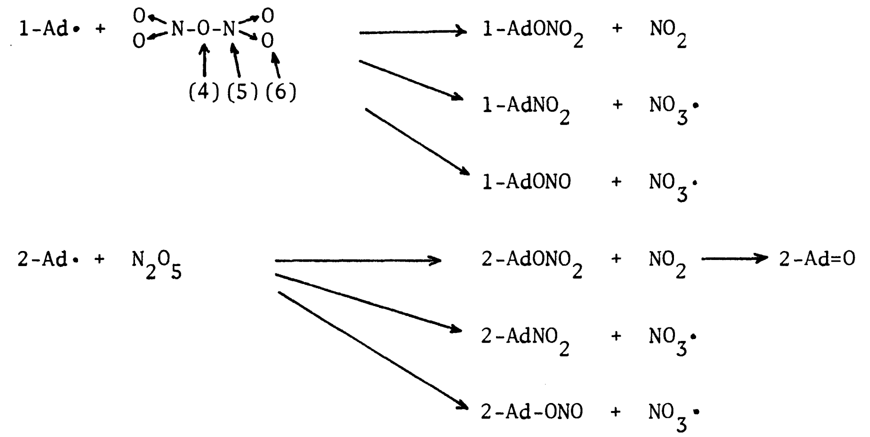
Initiation

$$N_2O_5 \xrightarrow{h\nu} {}^{S}(N_2O_5)^* \rightsquigarrow {}^{T}(N_2O_5)^* \longrightarrow NO_3\cdot + NO_2 \qquad (1)$$

$$NO_3\cdot + AdH \longrightarrow 1\text{-}Ad\cdot + 2\text{-}Ad\cdot + HNO_3 \qquad (2)$$

$$(NO_2)^* + AdH \xrightarrow[\text{(minor)}]{} 1\text{-}Ad\cdot + 2\text{-}Ad\cdot + HNO_2 \qquad (3)$$

Propagation



$$\text{1-Ad}\cdot + O_2N\text{-}O\text{-}NO_2 \longrightarrow \text{1-AdONO}_2 + NO_2 \qquad (4)$$

$$\longrightarrow \text{1-AdNO}_2 + NO_3\cdot \qquad (5)$$

$$\longrightarrow \text{1-AdONO} + NO_3\cdot \qquad (6)$$

$$\text{2-Ad}\cdot + N_2O_5 \longrightarrow \text{2-AdONO}_2 + NO_2 \longrightarrow \text{2-Ad=O} \qquad (7)$$

$$\longrightarrow \text{2-AdNO}_2 + NO_3\cdot \qquad (8)$$

$$\longrightarrow \text{2-Ad-ONO} + NO_3\cdot \qquad (9)$$

$$\text{1- or 2-AdONO} + N_2O_5 \longrightarrow \text{1- or 2-AdONO}_2 + 2NO_2 \qquad (10)$$

$$2NO_2 \xrightarrow{h\nu} 2NO + O_2 \qquad (11)$$

$$N_2O_5 + NO \longrightarrow NO_2 + NO + NO_3\cdot \qquad (12)$$

Although it was reported[9] that nitric oxide produced in the reaction (11) caused decomposition of N_2O_5 to produce NO_2 and O_2, we could not estimate the degree of the contribution of the reaction (11) and (12) in the present system.

Bridgehead to bridge reactivity ratio which was suggested to reflect the polarity and/or bulkiness[1] of the hydrogen abstracting species, is calculated to be 9 in the present reaction. This value is reasonable considering that the geometry of $NO_3\cdot$ was predicted from INDO calculation[10] to be Y shape (C_{2v} symmetry), non-bonded repulsion of which in the approach to bridge hydrogen was assumed to be relatively low.

ρ^* value was estimated to be -0.35 from the relative reactivity of bridgehead hydrogen between adamantane and carbomethoxyadamantane[11]. This value is comparable to that of $\cdot CCl_3$ (-0.42)[2], which suggests either (or both) that electron deficiency of $NO_3\cdot$ is similar to $\cdot CCl_3$ or (and) that $NO_3\cdot$ is so reactive as to make the transition state more shallow (more resembles to initial state) to reflect its electrophilicity.

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4. The ratio was determined with glpc. Before the ananlysis I was hydrolyzed in MeOH containing H_2SO_4 to the mixture of 1-adamantanol and 1-methoxyadamantane.
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11. In similar condition to adamantane, 1-carbomethoxyadamantane gave 1-carbomethoxy-3-adamantyl nitrate, 1-carbomethoxy-3-nitroadamantane,and 1-carbomethoxyketones (2-and 4-position) in a ratio of 2.7 : 1.0 : 2.7.

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