Comment on Conversion of Nitric Oxide into a Nitroxide Radical using 2,3-Dimethylbutadiene and 2,5-Dimethylhexadiene

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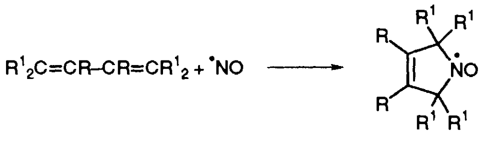
ESR spectroscopic evidence is given to suggest that NO_2 initiates radical formation instead of the previously assumed ring-closure mechanism in the reaction of nitric oxide with 2,3-dimethyl-1,3-butadiene and 2,5-dimethyl-2,4-hexadiene.

Gabr *et al.*[1] investigated reactions of nitric oxide with diolefins and suggested a ring closing reaction, eqn. (1).


(1)

1

The authors based this radical assignment on ESR spectra that manifested an additional hyperfine patterns of four hydrogens for $R_1 = H$, while for the case of $R_1 = Me$ only the nitrogen triplet could be seen. In our earlier work, where the nitric oxygen conversion into nitroxide were systematically studied,[2] we investigated the nitric oxide reactions with different mono-olefins. (The NO gas was formed by dropping conc. sulfuric acid into saturated water solution of $NaNO_2$. The reactor, where nitric oxide was generated, was flushed with argon prior to adding H_2SO_4). The olefins were dissolved in deaerated benzene. We observed—similarly to the classical analytical works of Brown[3]—no reactions if only pure NO was present, but a trace amount of NO_2 could catalyse nitroxide formation. The key step of this process is the nitroso (*pseudo*nitrosite) formation. The question can be raised: could this process explain the nitroxide formation for diolefins? In this case the first step is a reaction with NO_2 addition; eqn. (2).

$$R^1_2C{=}CR{-}CR{=}CR^1_2 + {\cdot}NO_2 \Rightarrow \underbrace{R^1_2(NO_2)C{-}CR{=}\dot{C}R{-}CR^1_2}_{X\cdot} \qquad (2)$$

that yields an alkyl radical, which subsequently can react with NO; eqn. (3),

$$X\cdot + NO\cdot \Rightarrow XNO \qquad (3)$$

and the nitroso could trap an alkyl radical; eqn. (4),

$$X\cdot + XNO \Rightarrow \underset{\mathbf{2}}{X_2NO\cdot} \qquad (4)$$

where **2** is a precursor of the crystalline X_2NOX end-product identified by Phillips and Coyne.[4]

No straightforward distinction between radicals **1** and **2** can be made by ESR hyperfine pattern, since in both cases a four-hydrogen-pattern is expected if R^1 is hydrogen, and only a nitrogen triplet can be observed if it is a methyl group. The hydrogen couplings, however, should be markedly different for these radicals owing to the conformation dependence *via* the well known dihedral relation, eqn. (5).

$$A = B_0 + B_2 \cos^2\theta \qquad (5)$$

where θ is the angle between planes p_zNC and NCH.

In the case of cyclic nitroxide, the rigid ring allows dihedral angles close to 30°, (we carried out a molecular mechanics calculations with PC-MODEL under normal RHF level, that yield θ values 22° and 38° for the respective hydrogens in the equilibrium conformation). By using usual parameter values (B_0 is small, B_2 is *ca.* 24 G) the hydrogen splitting is expected *ca.* 18 G, that is much larger than observed by Gabr *et al.*[1] (*i.e.* 10 G), and agrees with the value reported by Crayston *et al.*,[5] who very recently generated photochemically radical **1** by hydrogen abstraction from *N*-hydroxypyrrolidine (see Table 1). On the other hand for radical **2**, the sterically preferential conformation yields much larger dihedral angles (θ = 39 and 81°) and consequently smaller hyperfine splitting: A_H = 8 G. Since for open chain nitroxides restricted rotation occurs, the experimental splitting of 10 G is in accordance with this structure.

Table 1 Hyperfine parameters for radicals **1** and **2**

Radical	R^1	R	A_N/G	A_H/G	Amplitude variation	Ref.
1	H	Me	14.2	10	Yes	1
1	H	Me	14.7	18	No	5
1	Me	H	14.8	—	Yes	1
1	Me	H	14.3	—	No	6
2	Isobutylene		14.6	—	Yes	2
2	Styrene		15.0	12	Yes	2
2	Styrene		14.3	7	Yes	2

Another way of distinguishing radicals **1** and **2** can be made by linewidth analysis. In case of 2,5-dimethylhexadiene, the suggested radical **1** is exactly the same we have already synthesized and characterised by ESR spectroscopy.[6] For this radical we observed practically identical amplitudes in the nitrogen triplet that indicates fast rotation compatible with the small size of ring. The spectra presented in the paper of Gabr *et al.*,[1] however, show marked amplitude variation, the same as we found studying the nitric oxide reactions with olefins.[2] This fact implies that the observed radical should have a rather long chain, as in radical 2.

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