Mendeleev Commun., 1999, 9(2), 83–84

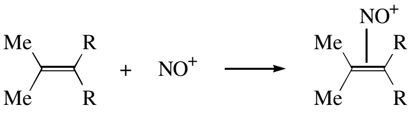
Interaction in olefin–NO$^+$ π-complexes: structure and dynamics of the NO$^+$–2,3-dimethyl-2-butene complex

Gennady I. Borodkin,* Innokenty R. Elanov, Alexander M. Genaev, Makhmut M. Shakirov and Vyacheslav G. Shubin

N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation. Fax: +7 3832 34 4752; e-mail: vshubin@nioch.nsc.ru

^{1}H and ^{13}C NMR studies involving the ^{13}C NMR deuterium perturbation method and *ab initio* calculations showed the interaction between 2,3-dimethyl-2-butene and the nitrosonium cation to form a dynamic π-complex.

Olefin–NO$^+$ π-complexes have often been postulated as intermediates in reactions of olefins with nitrosyl halides.[1,2] These reactions play an important role in the syntheses of various organic compounds such as nitroso and nitro halides,[1–4] aza heterocycles,[5] *etc*. However, available experimental data on these π-complexes are few in number (*cf*. refs. 6–8), and the fine structure of the complexes is obscure (*cf*. refs. 8, 9).

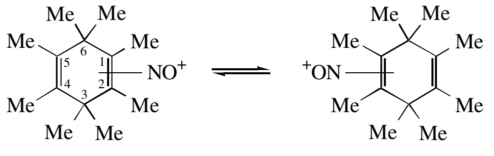


1a,**b** **2a**,**b**

a R = Me
b R = CD$_3$

Scheme 1

We examined the interaction of 2,3-dimethyl-2-butene **1a** with the NO$^+$ cation in low-nucleophilicity media at low temperatures in detail. The formation of a cationic complex between compound **1a** and the NO$^+$ cation was detected by the downfield shifts of the signals of C-2, C-3 and hydrogen atoms in the ^{13}C and ^{1}H NMR spectra, respectively (Table 1), when the olefin and NO$^+$AlCl$_4^-$ were mixed in SO$_2$–SO$_2$ClF–CD$_2$Cl$_2$ at –100 °C. The π-complex character of bonding in this cation follows from the consideration given below. The chemical shift of the signals of C-1 and C-5, as well as C-2 and C-4 atoms of the π-complex NO$^+$–octamethyl-1,4-cyclohexadiene **3**, which are 'averaged' owing to a degenerate rearrangement (Scheme 2), is 159.7 ppm.[6]

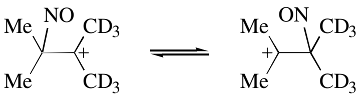


3 **3′**

Scheme 2

Assuming that the chemical shift of the C-4 and C-5 atoms of complex **3** is equal to that of the olefinic carbon atoms in the parent octamethyl-1,4-cyclohexadiene (129.7 ppm),[6] we come to the conclusion that the chemical shift of C-1 and C-2 atoms in complex **3** is to be 189.7 ppm (159.7×2 – 129.7). This value is very close to that found for the complex formed as a result of the interaction between olefin **1a** and the NO$^+$ cation (190.2 ppm).

We have obtained further evidence of the π-complex character of cation **2** using the isotope perturbation method.[10,11] The corresponding deuterated complex (as tetrachloroaluminate) was prepared from corresponding precursor **1b**† and NO$^+$AlCl$_4^-$ in SO$_2$–SO$_2$ClF–CD$_2$Cl$_2$. The ^{13}C NMR spectrum of this complex shows 'isotope splitting' ($\delta_{-100\,°C} = 1.1$ ppm), which does not correspond to an alternative version, namely, 'fluxional' σ-complex **4** (Scheme 3) (*cf*. refs. 10, 11).



4 **4′**

Scheme 3

In order to determine the fine structure of the olefin–NO$^+$ π-complexes, we performed *ab initio* calculations of the energy and chemical shift for complex **2a**. The geometry was optimized at the 6-31G* level using the GAMESS-94 program.[13] The results are indicative of the two modes of interaction of the nitrosonium cation with the olefin resulting in the formation of π-complexes: **A** (C_{2v} symmetry) and **B** (a little disturbed C_s symmetry). The Hessian analysis demonstrated that the structures **A** and **B** correspond to minima on the potential energy surface. These results are in accordance with those found earlier for the parent NO$^+$–ethylene model system.[9] Figure 1 represents the key geometrical features, Mulliken charges and bond orders. The heats of formation of the complexes **A** and **B** from olefin **1a** and NO$^+$ are 93.7 and 117.6 kJ mol^{-1} (exothermic reactions), and the distances between the N atom and the C$_2$–C$_3$ bond are 1.22 and 2.18 Å, respectively. In the π-complex **B**, the C–N bonds are very long (2.266 and 2.315 Å), and the bond orders are 0.293 and 0.272, respectively.

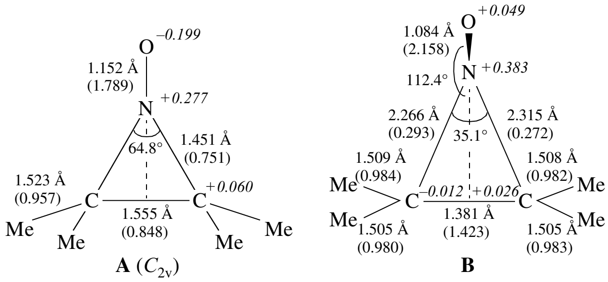


Figure 1 *Ab initio* optimized structures of the NO$^+$–2,3-dimethyl-2-butene complexes. Mulliken charges are italicised. Bond orders are given in parentheses.

Table 1 ^{1}H and ^{13}C NMR chemical shifts[a] for olefin **1** and NO$^+$–2,3-dimethyl-2-butene complexes.

Structure	Solvent[b]	T/°C	δ_H Me/ppm	δ_C/ppm	
				C-2 and C-3	Me
1a	SO$_2$–CD$_2$Cl$_2$	–70	1.48	133.3	20.1
1a	SO$_2$–SO$_2$ClF–CD$_2$Cl$_2$	–100	1.52	133.2	19.8
2a	SO$_2$–SO$_2$ClF–CD$_2$Cl$_2$	–100	2.37	190.2	18–28[c]
A[d]				67.2	17.6
B[d]				183.4, 189.8	21.9[e]

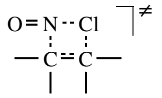
[a] Relative to Me$_4$Si with CH$_2$Cl$_2$ (^{1}H, δ 5.33 ppm) and CD$_2$Cl$_2$ (^{13}C, δ 53.6 ppm) as internal standards. [b] The SO$_2$–CD$_2$Cl$_2$ and SO$_2$–SO$_2$ClF–CD$_2$Cl$_2$ volume ratios are ~4:1 and ~1:2:1, respectively. [c] The exact chemical shift was not determined because the signal is masked by other signals of Me groups of polymeric products. [d] Shifts calculated by the IGLO method. [e] Averaged chemical shift.

---

† Olefin **1b** was prepared from [^{2}H$_6$]acetone and Pr^{i}MgI followed by dehydration of the resulting carbinol under the action of oxalic acid.[12]

The IGLO chemical shift DZ calculations[14] were performed using *ab initio* calculated geometries. Table 1 demonstrates that the chemical shifts of the C-2 and C-3 atoms in the complex **B** are equal to 183.4 and 189.8 ppm, respectively. The averaged value is very close to that found for -complex **2a**. The equivalence of the C-2 and C-3 atoms and also that of methyl groups observed in the ^{13}C NMR spectrum of -complex **2a** can be explained by fast inversion at the N atom or rotation of the NO group around the axis crossing the N atom and perpendicular to the C_2–C_3 bond and by fast migration of this group (*cf.* ref. 6).

It is well known that the addition of nitrosyl chloride to norbornene and other cyclic olefins in low-polarity solvents results in the formation of *syn*-adducts; skeletal rearrangements did not occur during the nitrosation.[2,15] A mechanism has been proposed[2,15] that involves a four-centre transition state of the type C.



C

Our results indicate that the absence of any skeletal rearrangement during nitrosation does not contradict the classical mechanism of the reaction[1,16] because the positive charge on basal carbon atoms in -complex intermediate **2** is very small. The capture of the chloride anion combined with cation **2** in a tight ion pair from the frontal side of the -complex is quite accessible, because the C–N bond orders in this complex are very small.

This work was supported by the Russian Foundation for Basic Research (grant no. 96-03-33333).

References

1 P. P. Kadzyauskas and N. S. Zefirov, *Usp. Khim.*, 1968, **37**, 1243 (in Russian).
2 P. B. D. de la Mare and R. Bolton, *Electrophilic Additions to Unsaturated Systems*, Elsevier, Amsterdam, 1982, p. 247.
3 F. Freeman, *Chem. Rev.*, 1975, **75**, 439.
4 A. V. Pankratov, *Khimiya Ftoridov Azota* (*Chemistry of Nitrogen Fluorides*), Khimiya, Moscow, 1973 (in Russian).
5 Q. B. Broxterman, H. Hogeveen, R. F. Kingma and F. van Bolhuis, *J. Am. Chem. Soc.*, 1985, **107**, 5722.
6 G. I. Borodkin, I. R. Elanov, V. A. Podryvanov, M. M. Shakirov and V. G. Shubin, *J. Am. Chem. Soc.*, 1995, **117**, 12863.
7 G. A. Olah, P. Schilling, P. W. Westerman and H. C. Lin, *J. Am. Chem. Soc.*, 1974, **96**, 3581.
8 E. Bosch and J. K. Kochi, *Res. Chem. Intermed.*, 1996, **22**, 209.
9 K. Raghavachari, W. D. Reents and R. C. Haddon, *J. Comput. Chem.*, 1986, **7**, 265.
10 P. E. Hansen, in *Ann. Rep. N.M.R. Spectrosc.*, Academic Press, London, 1983, vol. 15, p. 105.
11 H.-U. Siehl, in *Adv. Phys. Org. Chem.*, Academic Press, London, 1987, vol. 23, p. 63.
12 I. Schurman and C. E. Boord, *J. Am. Chem. Soc.*, 1933, **55**, 4930.
13 M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis and J. A. Montgomery, *J. Comput. Chem.*, 1993, **14**, 1347.
14 W. Kutzelnigg, U. Fleicher and M. Schindler, in *N.M.R. Basic Principles and Progress*, Springer, Berlin, 1991, vol. 23, p. 165.
15 D. L. H. Williams, *Nitrosation*, Cambridge University Press, Cambridge, 1988, p. 45.
16 C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, 1953.

Received: Moscow, 4th June 1998
Cambridge, 19th November 1998; Com. 8/04735I