

## Paradigms and paradoxes: energetics of the oxidative cleavage of azo compounds (diazenes)

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**Abstract** The enthalpy of oxidative cleavage of azo compounds (diazenes) is discussed and compared with that of symmetric olefins. The roles of substituents and of electronegativity are explicitly discussed.

**Keywords** Azo compounds · Oxidative cleavage · Enthalpy · Diazenes · Nitroso compounds · Singlet oxygen · Symmetric olefins

### Introduction

Recently [1] we discussed the energetics of the oxidative cleavage of symmetric olefins, i.e. the enthalpy of the formal reaction



These reactions (here limited to those in the gas phase) were shown to be always exothermic and spanned a nearly 400 kJ/mol range, from 212.5 kJ/mol for tetracyanoethylene to 589 kJ/mol for tetrafluoroethylene. Electron-withdrawing R and R' groups generally resulted in comparatively small enthalpies, electron-donating groups generally resulted in comparatively large enthalpies. What about the corresponding reaction of (generally gas phase) azo compounds, namely



For multiple reasons we expect to find a decreased exothermicity. The first harkens to Pauling's electronegativity equation (when expressed in kJ/mol) [2]

$$D[A-B] = \frac{1}{2}(D[A-A] + D[B-B]) + 96\Delta\chi \quad (3)$$

where the  $D$ s are bond energies and  $\Delta\chi$  is the difference of the electronegativities of  $A$  and  $B$ . (This equation has fallen into neglect, if not occasional disrepute. However, see the recent paper [2] and the corollary contained therein.) Applying this equation to doubly bonded species and recognizing  $\Delta\chi$  is smaller for the pair of atoms nitrogen and oxygen, than for carbon and oxygen, results immediately in the desired conclusion that reaction 2 will be less exothermic than reaction 1 for corresponding groups affixed to the double bond. One could compare the energetics of related compounds with C–C, O–O and hence C–O single bonds, with those of N–N, O–O and N–O single bonds. While there are numerous species for which the enthalpy of formation is known with C–C [3] and C–O [3] bonds, there are rather few with O–O single bonds [3]. Data for N–N single bond containing compounds are likewise scarce [3], for N–O all but nonexistent [3]. Alternatively, we recognize the reaction



is thermoneutral. O=O and O<sub>2</sub> are equated [4], in which nitrogen interpolates carbon and oxygen, again results in the prediction that reaction 2 will be less exothermic than reaction 1. What else can O=O be? It could be “singlet oxygen”, namely the <sup>1</sup>Δ low lying excited state. In this case, it is suggestive that O<sub>2</sub> should also be this state, even though that was not assumed in Ref. [1], and hence it will not be assumed here either.

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**Table 1** Enthalpy of formation of diverse azo compounds, RNNR and the corresponding nitroso species, RNO (all data in kJ/mol)

R	$\Delta H_f$ (RNNR)	Ref.	$\Delta H_f$ (RNO)	Ref.	$\Delta H_f$ (RNNR) – $2\Delta H_f$ (RNO)
H(g)	209 <sup>a</sup>	5	109 <sup>b</sup>	6	–9
CH <sub>3</sub> (g)	161 <sup>a</sup>	5	65	7	31
t-(CH <sub>3</sub> ) <sub>3</sub> C(g)	–36	3a	–29	7	22
C <sub>6</sub> H <sub>5</sub> (g)	404 <sup>c</sup>	8	209	7	14
(CH <sub>3</sub> ) <sub>2</sub> N(lq)	227	3a	5	9	217
(CH <sub>3</sub> ) <sub>2</sub> N(g)	271	3a	39	9 <sup>d</sup>	193
O <sup>–</sup> (aq)	–17	10	–105	9	193
OH(aq)	–64	10	–119	9	174
O-t-Bu(g)	–189	10	–172	11	155
F(g)	82 <sup>e</sup>	9	–67	9	216
Cl(g)	236 <sup>f</sup>	12	52	9	132

All azo compounds are taken as their E-isomer

<sup>a</sup> In the absence of unequivocal experimental findings, we use the result of G3 quantum chemical calculations of Ref. [5]. In Ref. [5], the Z-isomer of N<sub>2</sub>H<sub>2</sub> is found to be 21 kJ/mol less stable than the E-isomer

<sup>b</sup> In the absence of unequivocal experimental findings, we use the result of a CCSD (T) quantum chemical calculation in Ref. [6]

<sup>c</sup> This is the consensus value from the two contemporary studies, Ref. [8]a, b. The Z-isomer is 47 kJ/mol less stable, as derived from Ref. [8a]

<sup>d</sup> We derived the enthalpy of vaporization for dimethylnitrosamine as the average of the two quantities: that of dimethylformamide with which it is isoelectronic, and by assuming the difference of N-nitrosopiperidine and dimethylnitrosamine is the same as cyclohexanone and acetone (all ancillary data from Ref. [3a])

<sup>e</sup> This is for the less stable E-isomer (from Ref. [9]), this isomer was chosen because all the other azo compounds have this stereochemistry. The Z-isomer is 12 kJ/mol more stable than the E-isomer

<sup>f</sup> In the absence of experimental findings, we accept the results of CCSD(T)/CBS quantum chemical calculations in Ref. [12]. This is for the Z-isomer, the E-calculated to be 16 kJ/mol less stable

The current study provides a test of reaction 2 wherein all data will be for gas phase species unless otherwise said explicitly. For most of the species of interest there is no thermochemical information about the condensed phase, and for the one piece of data referring to aqueous species, there are no data for gases. Table 1 presents all the extant data known to the authors.

The pattern for the energetics of the oxidative cleavage of azo compounds corresponds to those found for the cleavage of olefins— $\pi$  donating groups are associated with large exothermicities is affirmed. It is pleasing that our expectation is realized that the exothermicities are smaller based on the increased electronegativity of C, N and O.

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