# REACTIVITIES OF DIETHYLHYDROXYLAMINE AND THIOLS TOWARDS EXCITED STATES OF ALKOXY AND ALKYL RADICALS: A COMPARISON

M.V. ENCINA, E. A. LISSI and H. SOTO

*Universidad Técnica del Estado, Departamento de Química, Facultad de Ciencia, Santiago (Chile)*

## Summary

The effect of diethylhydroxylamine and $n$-hexanethiol on the solution photolysis of several carbonyl compounds was investigated. Diethylhydroxylamine is more efficient as a singlet and triplet quencher than the thiol is. In contrast, $n$-hexanethiol is more efficient in trapping the 1,4-biradical produced in the photolysis of 5-methyl-2-hexanone. These results are discussed in terms of the relative reactivities of diethylhydroxylamine and $n$-hexanethiol towards alkyl and alkoxy radicals.

## 1. Introduction

The use of selective triplet quenchers has been one of the most powerful tools employed to elucidate the mechanisms and to evaluate the rates of photochemical reactions. An "ideal" selective triplet quencher should fulfil the following conditions: (1) it should have a high rate of quenching; (2) the rate of the process must be little dependent on the sensitizer employed (*i.e.* the process must be diffusion controlled); (3) interaction with the singlet must be negligible; (4) it should be transparent in the wavelength range considered; (5) it should not interfere with the analysis of the products. Most quenchers employed to study the photochemistry of carbonyl compounds (*i.e.* mono-olefins and di-olefins [1, 2] and aromatic compounds [3]) meet these conditions only partially. In particular the di-olefins, which are the most widely employed, are not suitable when compounds that give type I photocleavage are considered because of addition of the radicals produced to the quencher. The ideal quencher in this case will be a quencher which is totally inactive towards the radicals or which leads to simple products after reacting with the radicals. Among the more promising quenchers of the latter type are thiols [4, 5] and amines [6 - 8], in particular hydroxylamines [9]. Under suitable conditions these compounds can quantitatively transform

the radicals (R) produced into the corresponding hydrocarbon (RH), allowing $\phi_{cleavage}$ to be evaluated from $\phi_{RH}$.

In the present work we evaluated the reactivity of diethylhydroxyl-amine (DEHA) and $n$-hexanethiol towards several excited singlet and triplet states and towards the 1,4-biradical produced in the Norrish type II intra-molecular hydrogen abstraction. The results are discussed in terms of the reactivities of DEHA and $n$-hexanethiol towards alkyl and alkoxy radicals, which can be considered as suitable models for biradicals and $n\pi^*$ triplet excited states respectively.


## 2. Experimental

The experimental method employed was similar to that previously described [9]. Fluorescence measurements were carried out in a Hitachi–Perkin–Elmer 204-S spectrofluorimeter. Photochemical measurements were carried out at low conversion in a merry-go-round apparatus thermostatted at 20 °C. Product quantum yields were determined by gas–liquid chromatography employing suitable actinometers.

Methyl $tert$-butyl ketone was employed as a source of $tert$-butyl radicals. The quantum yield $\phi_{C_4H_{10}}$ was measured at 20 °C as a function of the ratio RH/isoprene (where RH is either a thiol or DEHA). At the concentrations of DEHA, isoprene and thiol employed these compounds quench neither the singlet nor the triplet excited states.

The pyrolysis of di-$tert$-butyl peroxide at 120 °C was employed as a source of $tert$-butoxy radicals. The ratio $tert$-butanol/acetone was measured as a function of RH concentration.

DEHA (Penwalt Co.) and $n$-hexanethiol (Eastman) were freshly distilled before use. All the reactants and solvents were of the highest purity com-mercially available. Most were further purified by distillation or recrystalliza-tion.

All determinations (with the exception of those noted in the text) were carried out using $n$-hexane as solvent.


## 3. Results

The values of the rate constants of the reaction

$$^1D + RH \xrightarrow{(k_q)_1} quenching \tag{1}$$

(where $D \equiv$ donor) can be directly derived from Stern–Volmer plots of the fluorescence quenching. The values of $(k_q)_1$ obtained employing $n$-hexane-thiol and DEHA are given in Table 1. In this table we have included previously reported data obtained in closely related systems.

**TABLE 1**

Singlet quenching

| Compound | $k_{DEHA}$ ($\times 10^7$ M$^{-1}$ s$^{-1}$) | $k_{R-SH}$ ($\times 10^7$ M$^{-1}$ s$^{-1}$) |
|---|---|---|
| Propanal[a] | 610 | 40 |
| 2-Methylpropanal | 570 | <10 |
| Pentanal | 490 | <10 |
| Acetone[a] | 390 | 40 |
| Cyclopentanone | 350 | — |
| 2-Pentanone | 240 | — |
| 2-Methylcyclohexanone | 210 | — |
| 3-Pentanone | 200 | — |
| 2-Butanone | 190 | — |
| 2,4-Dimethyl-3-pentanone | 180 | 20 |
| 3-Methyl-2-butanone | 170 | — |
| 3,3-Dimethyl-2-butanone | 110 | 20 |
| 2,2,4,4-Tetramethyl-3-pentanone | 90 | — |
| Biacetyl | 550 | <10 |
| Methyl pyruvate[b] | 210 | 220 |
| Naphthalene | 100 | <1 |
| Benzil | 430 | <5 |

[a]Data taken from ref. 2.
[b]Data taken from ref. 10.


The method employed to obtain the values of the rate constant for the triplet quenching

$$^3D + RH \rightarrow \text{quenching} \qquad (2)$$

depends on the characteristics of the system. If the compound considered phosphoresces (*e.g.* biacetyl) the value can be obtained from a Stern–Volmer plot of the phosphorescence intensities. For the remaining compounds the values were derived from the change in product quantum yield as a function of added RH. In this case the possibilities that the product considered could be formed from the singlet (*i.e.* in aliphatic ketones) and that RH could interfere with an intermediate (*i.e.* the triplet biradical in type II processes) must be considered. Table 2 gives the values of $k_q$ measured from the change in phosphorescence intensities. Table 3 gives the values of the slopes of the Stern–Volmer plots obtained from the change in product quantum yield arising from the triplet states.

The effect of isoprene on the isobutane quantum yield from the photolysis of methyl *tert*-butyl ketone in the presence of RH (either DEHA or the thiol) allows $(k_{RH}/k_{isoprene})_{tert-butyl}$ to be evaluated. Similarly, the dependence of $\phi_{tert\text{-butanol}}/\phi_{acetone}$ on the RH concentration in the pyrolysis of di-*tert*-butyl peroxide allows $(k_{RH}/k_{fragmentation})_{tert-butoxy}$ to be evaluated. Secondary reactions of the radicals in the presence of DEHA and thiols can be disregarded since $\phi_{acetone} + \phi_{tert\text{-butanol}}$ remains independent of the RH concentration. The values obtained are given in Table 4. The results show that *n*-hex-

TABLE 2

Quenching of phosphorescence intensity

| | $k_q$ (×$10^7$ M$^{-1}$ s$^{-1}$) | |
| --- | --- | --- |
| | *DEHA* | *n-Hexanethiol* |
| Biacetyl | 3 | —[a] |
| Benzil | 70 | —[a] |
| Benzophenone[b] | 170 | 1.3 |

[a]The quenching of biacetyl and benzil for the thiol shows
an erratic behaviour and does not allow the evaluation of $k_q$.
[b]In benzene.

TABLE 3

Quenching of the quantum yield product from the triplet state

| | $\tau_T$ (ns) | $\tau_{biradical}$ (ns) | *Stern–Volmer slopes* (M$^{-1}$) | |
| --- | --- | --- | --- | --- |
| | | | *DEHA* | *n-Hexanethiol* |
| 4-Methyl-2-pentanone | 126 | | 240 | 27 |
| 2-Heptanone | 2.4 | | 12 | — |
| 5-Methyl-2-hexanone | 1.0 | 4000[a] | Not measurable | 15.2 |
| β-Methylbutyrophenone | 50.0 | 40[b] | 280 | — |
| γ-Methylvalerophenone | 2.0 | 40[b] | Not measurable | — |

[a]Data taken from ref. 11.
[b]Data taken from ref. 12.

TABLE 4

Reactivities of DEHA and n-hexanethiol towards *tert*-butyl and *tert*-butoxy radicals

| | $(k_{RH}/k_{isoprene})_{tert\text{-}butyl}$[a] | $(k_{RH}/k_{fragmentation})_{tert\text{-}butoxy}$[b] |
| --- | --- | --- |
| DEHA | 1.2 | 840 |
| n-Hexanethiol | 10.9 | 19.5 |

[a]At 20 °C in n-hexane.
[b]At 120 °C in benzene as solvent.

anethiol is nearly 10 times more reactive than DEHA towards *tert*-butyl radicals (at 20 °C). In contrast, when *tert*-butoxy radicals are considered, DEHA is considerably more reactive than the thiol (nearly 40 times at 120 °C).

   The isopropanol quantum yield in the photolysis of acetone in n-hexane was determined in the presence of 0.04 M DEHA. The value of $\phi_{propanol}$ depends on the irradiation time, but the extrapolation to very short times gives $\phi_{propanol} = 0.93$.

# 4. Discussion

## 4.1. Singlet quenching

The results given in Table 1 show that for all donors except methyl pyruvate [10], DEHA is much more efficient than $n$-hexanethiol as a singlet quencher. The results obtained for DEHA and the monocarbonyl donors show that $k_{DEHA}$ decreases as $\alpha$ substitution increases. This dependence can be explained either in terms of steric hindrance or as an effect due to a decrease in the electronic affinity of the donors [13]. The latter possibility is based on the assumption that charge transfer is significant in the stabilization of the intermediates (or activated complexes) leading to quenching. This is supported by the results obtained employing amines and $tert$-butoxy radicals which show that even in a "radical-like reaction" charge delocalization plays a significant role [14]. Similarly, the large value obtained employing naphthalene indicates that DEHA is able to quench excited singlets by a charge transfer mechanism. Nevertheless, it is interesting to note that naphthalene is quenched faster by triethylamine and diethylamine than by DEHA, a result which indicates that DEHA has a higher ionization potential. In contrast, the quenching of biacetyl and acetone singlets by DEHA is considerably faster than that reported for the amines [6, 7]. This emphasizes the contribution of the DEHA labile hydrogen (dissociation energy 69.5 kcal $mol^{-1}$ [15]) to the deactivation process.

For most compounds the quenching of the singlets by $n$-hexanethiol is considerably slower than that obtained employing DEHA. Similar results were obtained for the quenching of the excited triplets (see Tables 2 and 3). It is difficult to find the origin of this difference, but a smaller tendency to give charge transfer complexes (see quenching by naphthalene), a reduced rate of hydrogen transfer (due to the larger bond dissociation energy (approximately 89 kcal $mol^{-1}$ [16])) and the reduced reactivity towards alkoxy radicals (see Table 4) could explain it.

## 4.2. Triplet quenching

The results given in Table 3 show noticeable differences between DEHA and $n$-hexanethiol as quenchers. DEHA is a "normal" quencher and the values of $k_q \tau_T$ decrease for a given type of carbonyl compound as the triplet lifetime decreases. This dependence is considerably smaller when the thiol is employed.

This result suggests that in the photolysis of 5-methyl-2-hexanone and $\gamma$-methylvalerophenone the thiol is mainly trapping the 1,4-biradical. However, at least when the photochemistry of ketones bearing primary and secondary $\gamma$ hydrogens is considered, it can be concluded that DEHA interacts almost exclusively with the excited triplets. The values of $(k_q)_T$ and $k_{biradical}$ obtained from these considerations are given in Table 5. In this table values of $k_{biradical}$ obtained directly by monitoring the decay of the biradical triplet in the presence of octanethiol [5] have also been included.

TABLE 5

Rate constants for the quenching of the triplet state and the type II biradicals

| Compound | $k_T$ ($\times 10^7$ $M^{-1}$ $s^{-1}$) | | $k_{biradical}$ ($\times 10^7$ $M^{-1}$ $s^{-1}$) | |
|---|---|---|---|---|
| | DEHA | RSH | DEHA | RSH |
| 4-Methyl-2-pentanone | 190 | <21 | — | — |
| 2-Heptanone | 240 | — | — | — |
| 5-Methyl-2-hexanone | — | — | <0.15 | 0.4 |
| β-Methylbutyrophenone | 560 | — | — | — |
| Valerophenone | — | — | — | 1.1[a] |
| γ-Methylvalerophenone | — | — | — | 0.9[a] |
| Acetophenone | — | 1.4[b] | — | — |

[a]Octanethiol as RSH. Measured from the change in the biradical lifetime [5] in 1.2 M pyridine with benzene as solvent.
[b]Data taken from ref. 17.

The data given in Tables 2 and 5 show that DEHA is more reactive than the thiol towards excited n$\pi^*$ singlets and triplets. These results are similar to those obtained when the alkoxy radicals are considered and can be rationalized in terms of a particularly large rate of hydrogen abstraction from DEHA by oxygen-centred radicals [18]; this is favoured both by the low dissociation energy of the O—H bond in DEHA [15] and by the small repulsion expected between the two oxygen atoms along the reaction coordinate [19]. For the reaction of the thiols, both the higher dissociation energy and the larger repulsion expected between the oxygen and sulphur atoms along the reaction path could explain their smaller rate of hydrogen abstraction [19, 20].

The results obtained employing DEHA can be rationalized in terms of the energy of the triplet and the stabilization energy of the radical produced [20, 21]. This result, as well as the large photoreduction quantum yield obtained in the photolysis of acetone, indicates that triplet quenching by DEHA of n$\pi^*$ states can be considered as a "radical-like" process leading to the stabilized diethyl nitroxide radical. Furthermore, it is interesting to note that the "radical-like" reactivity of acetophenone and benzophenone towards thiols can be even lower than that suggested by the $(k_q)_T$ values given in Table 5 since the quenching process takes place, at least partially, at the non-bonding electrons of the sulphur atom [22].

Regarding the tert-butyl radical and the 1,4-biradicals, n-hexanethiol reacts faster than DEHA does. These relative reactivities are opposite to those expected from thermochemical considerations and emphasize the role played by other factors in determining the rate of hydrogen abstraction. In particular, a larger repulsion between the oxygen and carbon atoms in the DEHA reaction could explain, at least partially, the reduced reactivity of these compounds towards the alkyl radicals. In this regard it is interesting to note that a C—O bond is nearly 8 kcal mol$^{-1}$ stronger than a similar C—S bond [16].

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