

RADICAL SCAVENGING AND EXCITED STATE QUENCHING EFFICIENCY OF ADDITIVES IN THE PHOTOCHEMISTRY OF ACETONE

G. LENDVAY and T. BÉRCES

Central Research Institute for Chemistry, Hungarian Academy of Sciences,
Pusztaszeri ut 59/67, H-1025 Budapest (Hungary)

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Summary

The effect of hydrogen sulphide, ethanethiol, diethyl sulphide and diethylhydroxylamine on the gas phase photolysis of acetone has been studied. Diethylhydroxylamine was found to be much more reactive than thiols and thioethers towards the $n\pi^*$ triplet state of acetone. However, H_2S and C_2H_5SH proved to be more effective methyl-radical trapping agents than diethylhydroxylamine. The following kinetic data were determined for hydrogen-atom abstractions by CH_3 from C_2H_5SH and $(C_2H_5)_2NOH$ respectively:

$$\log(k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = \frac{(8.4 \pm 0.4) - (9.7 \pm 0.3)}{RT \ln 10} \text{ kJ mol}^{-1}$$

$$\log(k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = \frac{(8.0 \pm 0.4) - (12.7 \pm 2.6)}{RT \ln 10} \text{ kJ mol}^{-1}$$

These data were used to characterize the radical scavenging efficiencies of the thiol and hydroxylamine compounds, while quenching data indicated the triplet quenching efficiencies of the substrates studied.

1. Introduction

Determination of the primary quantum yield of type I photolysis for aliphatic ketones requires the elucidation of the mechanism of the secondary processes which follow dissociation into free radicals. In principle, the sequence of secondary free radical processes can be simplified and as a result the determination of the primary quantum yield may be made more straightforward by using radical scavengers. However, the application of the radical-trapping technique is often complicated by the excited state quenching

effect caused by the radical scavenger. An ideal selective radical scavenger should exert no excited state quenching effect when applied at a concentration which is sufficiently high to trap practically all of the free radicals formed in the primary photochemical process.

Various additives have been used as radical scavengers in the photolysis of acetone, *e.g.* iodine [1], hydrogen bromide [2], hydrogen iodide [3] etc. The effect of diethylhydroxylamine and thiol additives in the photolysis of several carbonyl compounds has also been considered [4]. In the present study we report on the free-radical trapping and triplet state quenching efficiencies of hydrogen sulphide, ethanethiol and diethylhydroxylamine. The effect of the additives has been investigated in the vapour phase photolysis of acetone. The rate of hydrogen-atom abstraction by methyl radicals from the additive is used to express the radical-trapping efficiencies, while the effect on the acetone phosphorescence lifetime is taken as a measure of the triplet-quenching efficiencies of the additives.

2. Experimental details

2.1. Technique

Quantum yields were determined by conventional steady state photolysis experiments. A parallel light beam of wavelength 313 nm from an Osram HBO super-pressure mercury arc equipped with a filter combination (described elsewhere [5]) was used for irradiation. Light intensities were measured with a photocell calibrated by ferrioxalate actinometry. The rate of light absorption was calculated using experimentally obtained values for the molar extinction coefficient of acetone. The latter was found to be given as a function of temperature by $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1} = (7.9 \times 10^{-3}T - 0.33)$, where T designates the temperature in kelvin. The vapour mixture, composed of the degassed starting materials, was irradiated in a cylindrical quartz cell of 4.0 cm internal diameter and 5.0 cm length surrounded by a thermostat jacket. Photolysed samples were analysed by gas chromatography using perfluorocyclobutane as internal standard. Separation was executed on a 2 m alumina column at 60 °C.

Triplet lifetimes were derived from phosphorescence measurements made with an apparatus consisting of a nanosecond flash lamp, an optical detection system (Applied Photophysics, London) an ICA-70 type multichannel analyser (KFKI, Budapest) and a microcomputer. The multichannel analyser was used in its multiscaling mode with a channel width of 5 μs .

2.2. Materials

Acetone (Carlo Erba Spectroscopic Grade), characterized by its phosphorescence lifetime of 1.95×10^{-4} s at 100 Torr, was used without further purification. Diethylhydroxylamine (EGA-Chemie), ethanethiol (technical grade) and diethyl sulphide (technical grade) were purified by vacuum distillation and their quality was checked by gas chromatography.

3. Results and discussion

3.1. Quantum yields of methyl-radical formation

Provided that the reaction mechanism is known, quantum yields for methyl-radical formation can be derived from measurements of the steady state product yields of acetone photolysis with and without additives.

The simple mechanism presented in Scheme 1 explains our observations and can serve as the basis of the following discussion. Reactions (1) - (9) are the photophysical and photochemical processes which occur in the absence of additives. For simplicity, all the events that take place between absorption of the photon and formation of the triplet molecule are represented by process (1). Similarly, process (2) represents all reactions consuming triplet acetone except type I decomposition into CH_3 and CH_3CO radicals and triplet state quenching by the additive.



Scheme 1.

Additional reactions that occur in the system when acetone is photolysed in the presence of an additive QH are given by steps (10) - (12). In adopting the submodel of reactions induced by QH, a few assumptions are made: (i) the additive QH may quench the triplet state physically or chemically, and both types are represented by process (10); (ii) methyl radicals are scavenged efficiently by the additives, but hydrogen-atom abstraction from QH by CH_3CQ is insignificant both at low temperatures (because of a high activation energy) and at higher temperatures (because of fast competing decomposition of CH_3CO); (iii) radical Q disappears from the system without significant interaction with CH_3 and CH_3CO (some of the CH_3CO

radicals may be removed by combination with $(C_2H_5)_2NO$ at low temperatures; however, the effect on our results is expected to be small).

Quantum yields of product formation in the photolysis of acetone containing ethanethiol have been determined over the temperature range of 301 - 358 K. The acetone concentration was fixed throughout the series at a value of $7.5 \times 10^{-3} \text{ mol dm}^{-3}$, while the C_2H_5SH concentration was varied from 0 to $5 \times 10^{-5} \text{ mol dm}^{-3}$. The quantum yields of the two major photolysis products, CH_4 and C_2H_6 , are given as a function of C_2H_5SH concentration for 318 K in Fig. 1. As expected on the basis of the methyl-radical scavenging effect of the thiol, methane yields increase with increasing C_2H_5SH concentration up to a limiting value, while ethane yields decrease simultaneously and attain a negligibly small value. Apart from the smallest thiol concentrations, the sum $\Phi(CH_4) + 2\Phi(C_2H_6)$ is found to be practically constant. Similar observations were also made at 301, 337 and 358 K. However, the limiting value of $\Phi(CH_4)^{\text{max}}$ is 0.24 at 301 K, 0.75 at 318 K, 1.32 at 337 K and 2.00 at 358 K. The behaviour of the quantum yields of CH_4 and C_2H_6 formation and especially the constancy of $\Phi(CH_4) + 2\Phi(C_2H_6)$ over most of the C_2H_5SH concentration range indicates that quenching of triplet acetone is negligible at the additive concentrations studied. Moreover, the results indicate that C_2H_5SH is a very efficient methyl-radical scavenger and practically all methyl radicals are converted to methane at sufficiently high ethanethiol concentrations.

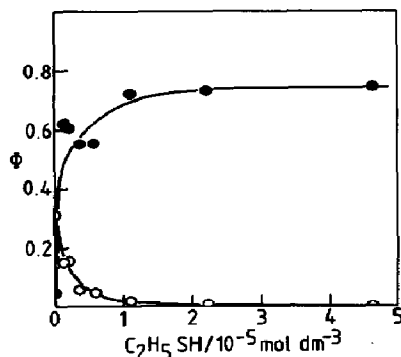


Fig. 1. Product quantum yields as a function of C_2H_5SH concentration in the photolysis of acetone at 318 K: ●, $\Phi(CH_4)$; ○, $\Phi(C_2H_6)$.

The quantum yield of methyl-radical formation can be given by the yields of CH_4 and C_2H_6 formation as

$$\phi(CH_3) = \frac{\Phi(CH_4) + 2\Phi(C_2H_6)}{\alpha} \quad (13)$$

where α designates that proportion of the methyl radicals which react under the given conditions by forming CH_4 and C_2H_6 product. According to Scheme 1, α may be expressed by the ratio of reaction product yields:

$$\alpha = \frac{\Phi(\text{CH}_4) + 2\Phi(\text{C}_2\text{H}_6)}{\Phi(\text{CH}_4) + 2\Phi(\text{C}_2\text{H}_6) + \Phi(\text{CH}_3\text{COCH}_2) + \Phi(\text{CH}_3\text{COC}_2\text{H}_5)} \quad (14)$$

Moreover, the quantum yield of methyl-radical formation, $\phi(\text{CH}_3)$, is related to the primary quantum yield of type I photodecomposition of acetone into CH_3 and CH_3CO , ϕ_1^0 , by the equation

$$\phi_1^0 = \frac{\phi(\text{CH}_3)}{1 + \beta} \quad (15)$$

where β is the proportion of acetyl radicals decomposing into CH_3 and CO in reaction (4), *i.e.*

$$\beta = \frac{\Phi(\text{CO})}{\Phi(\text{CO}) + \Phi(\text{CH}_3\text{COCH}_3) + 2\Phi(\text{CH}_3\text{CO})_2} \quad (16)$$

These generally valid relations indicate that the methyl-radical yield $\phi(\text{CH}_3)$ (which is closely related to the primary quantum yield of type I decomposition) can be derived from experiments carried out under experimental conditions where $\alpha \approx 1$ or where α assumes a known value. At sufficiently high ethanethiol concentrations $\alpha^\infty \approx 1$ and

$$\phi^0(\text{CH}_3) \approx \Phi^\infty(\text{CH}_4) + 2\Phi^\infty(\text{C}_2\text{H}_6) \approx \Phi^\infty(\text{CH}_4) \quad (17)$$

The quantum yields of methyl-radical formation derived according to eqn. (17) are summarized in Table 1. The value of β^∞ ($0 \leq \beta^\infty \leq 1$) strongly depends on the reaction temperature and it is only at low temperature that $\beta^\infty \approx 0$ and hence $\phi_1^0 \approx \Phi^\infty(\text{CH}_4)$.

TABLE 1

Quantum yields of methyl radical formation derived according to eqn. (17)

	Temperature (K)			
	301	318	337	358
$\phi^0(\text{CH}_3)$	0.24	0.75	1.32	2.00

With decreasing ethanethiol concentration, the CH_3 radical concentration increases, which favours radical combination reactions causing α to be less than unity. Thus

$$\phi^0(\text{CH}_3) > \Phi(\text{CH}_4) + 2\Phi(\text{C}_2\text{H}_6) \quad (18)$$

At the same time, β also decreases and no reliable estimation of ϕ_1^0 can be derived from results obtained at low additive concentrations.

The quantum yield $\phi(\text{CH}_3)$ of methyl-radical formation, derived according to eqn. (17) from the high thiol concentration limiting value of the methane yield, is given as a function of temperature in Fig. 2. The results clearly indicate the strong temperature dependence of the quantum yield of

methyl-radical formation. $\phi(\text{CH}_3)$ approaches the theoretical limit of 2 above about 90 °C. (Note that the 85 °C value of $\phi(\text{CH}_3)$ is probably an over-estimation.) The temperature dependence of $\phi(\text{CH}_3)$ may originate partly from the dependence of the primary type I decomposition yield ϕ_1^0 on temperature and partly from the increase in β with temperature. We have also given in Fig. 2 the Φ_1^0 values as reported by Larson and O'Neal [2]. These results show that a considerable part of the increase in the quantum yield of methyl-radical formation with temperature comes from the temperature dependence of the primary decomposition yield. In principle, a comparison of the $\phi(\text{CH}_3)$ and ϕ_1^0 results should give, according to eqn. (15), the proportion β of the acetyl radicals decomposed as a function of temperature. However, the experimental errors appear to be too large to supply reliable quantitative results for β and its temperature dependence.

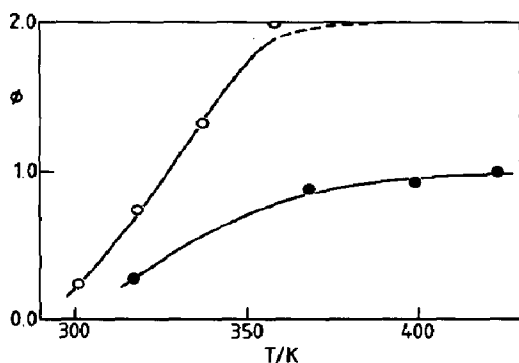


Fig. 2. Quantum yields: \circ , methyl radical formation derived from experiments made with added ethanethiol; \bullet , primary type I decomposition reported by Larson and O'Neal [2].

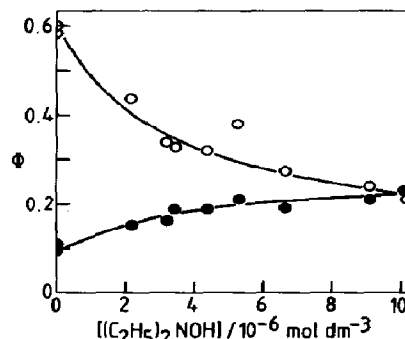


Fig. 3. Product quantum yields as a function of $(\text{C}_2\text{H}_5)_2\text{NOH}$ concentration in the photolysis of acetone at 345 K: \bullet , $\Phi(\text{CH}_4)$; \circ , $\Phi(\text{C}_2\text{H}_6)$.

Quantum yields of product formation in the photolysis of acetone containing diethylhydroxylamine have been determined over the temperature range 298 - 430 K. The acetone concentration was $7.5 \times 10^{-3} \text{ mol dm}^{-3}$ and the additive concentration was varied from 0 to $1 \times 10^{-5} \text{ mol dm}^{-3}$ in the reaction series. The dependence of CH_4 and C_2H_6 yields on diethylhydroxylamine concentration at 345 K is demonstrated in Fig. 3. Although these results obtained with added hydroxylamine show certain similarities to the thiol plots, the sum of the product yields here, $\Phi(\text{CH}_4) + 2\Phi(\text{C}_2\text{H}_6)$, is not, however, constant but decreases with increasing additive concentration. This decrease may be interpreted as a result of acetone triplet state quenching by diethylhydroxylamine. A definite sign of the triplet-quenching effect may also be detected at 298, 325, 364, 400 and 430 K in the reaction series carried out with added diethylhydroxylamine.

The effect of diethylhydroxylamine on the yields of the major products may be well represented by $\{\Phi'(\text{CH}_4) + 2\Phi'(\text{C}_2\text{H}_6)\}^{-1}$ vs. $[\text{QH}]$ plots, where Φ' represents the product quantum yields determined in the presence of

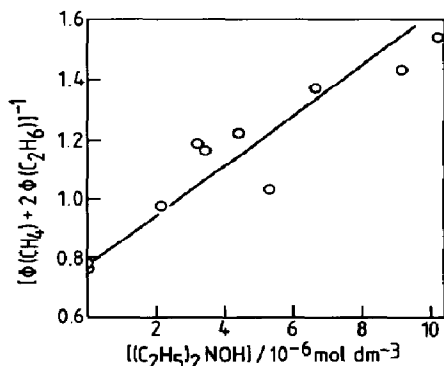


Fig. 4. Quenching plots of photolysis products as a function of $(C_2H_5)_2NOH$ concentration at 345 K.

triplet state quenching additives. Such plots of the 345, 364, 400 and 430 K results were found to give good straight lines, as shown for 345 K in Fig. 4. Deviations from the straight line are observed, however, at lower temperatures (at 325 and 298 K).

Considering the conditions where $\{\Phi'(CH_4) + 2\Phi'(C_2H_6)\}^{-1}$ vs. $[QH]$ plots may give straight lines, one can easily derive the correlation

$$\frac{1}{\Phi'(CH_4) + 2\Phi'(C_2H_6)} = \frac{\alpha}{\alpha'} \frac{1 + \beta}{1 + \beta'} \frac{1}{\Phi(CH_4) + 2\Phi(C_2H_6)} (1 + k_{10}^3 \tau_0 [QH]) \quad (19)$$

Here α' is the proportion of CH_3 radicals reacting to form CH_4 or C_2H_6 products in the presence of the triplet-quenching additive QH , while β' is the proportion of CH_3CO radicals decomposing according to reaction (4) into $CH_3 + CO$ in the presence of the QH additive. If $(\alpha/\alpha')(1 + \beta)/(1 + \beta')$ is approximately constant and close to unity in the reaction series carried out with diethylhydroxylamine additive, the experimental results are expected to satisfy Stern–Volmer-type straight-line correlations. It is probable that the conditions $\alpha' \approx \alpha$ and $\beta' \approx \beta$ are met especially at higher temperatures where most of the CH_3 radicals are recovered in the form of CH_4 and C_2H_6 and where the fate of most acetyl radicals is decomposition to the products CH_3 and CO . However, the conditions $\alpha' < \alpha$ and $\beta' < \beta$ are expected at the lower temperatures (and at relatively high light intensities) where radical–radical reactions dominate and a substantial part of the CH_3 and CH_3CO radicals may be removed by combination routes such as reactions (6), (7), (9) etc. Indeed, the observations are in accordance with these expectations; thus we shall use eqn. (19) to derive quantitative data for $\Phi(CH_4) + 2\Phi(C_2H_6)$ and the quenching constant $k_{10}^3 \tau_0$ above 340 K, and to make estimations of these quantities at 325 K.

From the intercepts of the straight lines plotted according to eqn. (19), data for $\alpha\phi^0(CH_3)$ are obtained which are presented, as a function of temperature, in Fig. 5 (open circles) and are listed in Table 2. For comparison, a similar quantity of $\Sigma\Phi(\text{product}) = \Phi(CH_4) + 2\Phi(C_2H_6) + \Phi(CH_3COC_2H_5)$,

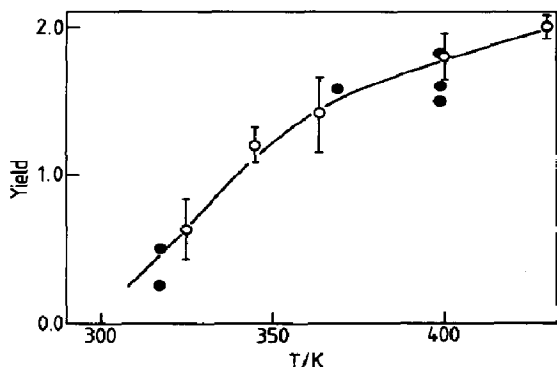


Fig. 5. Quantum yields: \circ , $\alpha\phi^0(\text{CH}_3)$ yields derived from experiments made with added diethylhydroxylamine; \bullet , $\Sigma\Phi(\text{product}) = \Phi(\text{CH}_4) + 2\Phi(\text{C}_2\text{H}_6) + \Phi(\text{CH}_3\text{COC}_2\text{H}_5)$ product yields calculated from the data of Larson and O'Neal [2].

TABLE 2

Methyl yields and quenching constants derived from diethylhydroxylamine experiments

	Temperature (K)				
	325	345	364	400	430
$\alpha\phi^0(\text{CH}_3)$	≈ 0.6	1.2 ± 0.2	1.4 ± 0.3	1.8 ± 0.2	≈ 2.0
$k_{10}^3\tau_0 (10^4 \text{ mol dm}^{-3})$	≈ 40	8.5 ± 2.0	2.3 ± 0.7	2.3 ± 0.7	≈ 4

calculated from the results of Larson and O'Neal [2], is also given in Fig. 5.

Since the quantum yield of methyl-radical formation $\phi^0(\text{CH}_3)$ could be derived from the thiol investigations and $\alpha\phi^0(\text{CH}_3)$ was obtained from the experiments carried out with hydroxylamine, comparison of the two sets of data supplies information on the importance (*i.e.* the quantum yield and temperature dependence) of higher molecular weight products formed in methyl-radical reactions (see Fig. 6). The proportion of CH_3 radicals forming

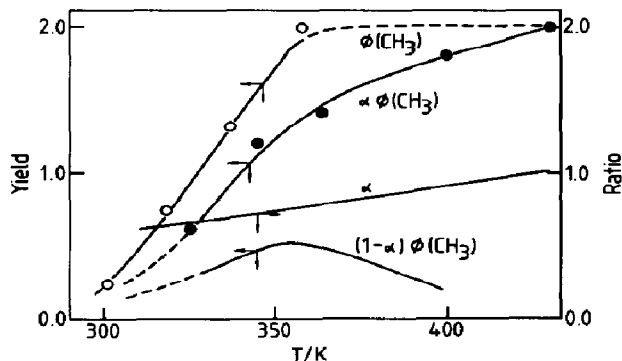


Fig. 6. Methyl-radical yields and ratios expressing the importance of different reaction routes of methyl radicals.

CH_4 or C_2H_6 , designated by α , is seen to increase steadily from about 0.66 at 300 K to a value above 0.95 at 425 K. However, $(1 - \alpha)\phi(\text{CH}_3)$, i.e. the yield of CH_3 radicals which react to re-form CH_3COCH_3 or to give $\text{CH}_3\text{-COC}_2\text{H}_5$, changes according to a function showing a maximum around 360 K. The initial increase in $(1 - \alpha)\phi(\text{CH}_3)$ is caused by the rapid increase with temperature in the yield of CH_3 formation, while the decrease reflects the fact that $(1 - \alpha)$ vanishes at higher temperatures.

3.2. Rate coefficients for hydrogen-atom abstraction by methyl radicals

Rate coefficients for metathesis reactions between CH_3 radicals and QH additives have been determined using the kinetic technique of competitive reactions. From the reactions in Scheme 1 one obtains the relationship

$$\frac{R(\text{CH}_4)}{R^{1/2}(\text{C}_2\text{H}_6)} = \frac{k_8}{k_5^{1/2}} [\text{CH}_3\text{COCH}_3] + \frac{k_{11}}{k_5^{1/2}} [\text{QH}] \quad (20)$$

The rate coefficient ratio $k_{11}/k_5^{1/2}$ was obtained from the slope of plots of

$$\frac{R(\text{CH}_4)}{R^{1/2}(\text{C}_2\text{H}_6)} - \frac{k_8[\text{CH}_3\text{COCH}_3]}{k_5^{1/2}} \text{ vs. } [\text{QH}]$$

where literature data were used for k_8 [6] and k_5 [7]. Eventually, the value of k_{11} (which indicates how efficient a CH_3 -trapping agent the additive QH is) could be derived from the rate coefficient ratio by means of k_5 taken from the literature.

As a test of our experimental technique, a few experiments were carried out with a hydrogen sulphide additive which gave $(2.9 \pm 0.3) \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for the rate coefficient of the metathesis reaction between CH_3 and H_2S at 298 K. Kinetic data reported in the literature yield for the same rate coefficient at room temperature $(3.0 \pm 0.2) \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [8] and $(2.1 \pm 1.5) \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [9], in excellent agreement with the figure obtained in the present work.

Systematic studies were carried out with ethanethiol and diethylhydroxylamine. In this series of experiments, the acetone concentration was $7.5 \times 10^{-3} \text{ mol dm}^{-3}$ and the additive concentration was varied. Plots according to eqn. (20) gave good straight lines over all experimental conditions studied.

The temperature dependence of the rate coefficients for hydrogen-atom abstraction from ethanethiol by methyl radicals is given in an Arrhenius form in Fig. 7. Weighted least-squares fitting of the data measured over the temperature range of 301 - 358 K yields

$$\log(k_{11}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = \frac{(8.4 \pm 0.4) - (9.7 \pm 0.3)}{RT \ln 10} \text{ kJ mol}^{-1} \quad (21)$$

where the error limits are standard deviations. From eqn. (21) one calculates $k_{11} = 5.0 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for 298 K which is more than two orders of magnitude higher than the room temperature value ($3.5 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) reported for this reaction by Kerr and Trotman-Dickenson [10]. Conse-

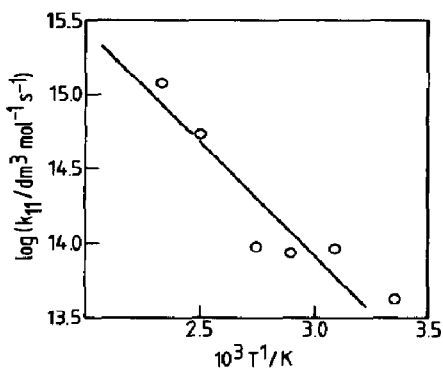
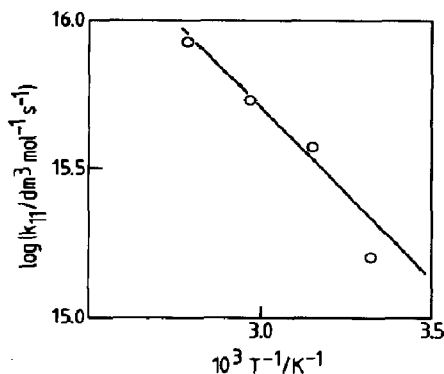


Fig. 7. Arrhenius plot for hydrogen-atom abstraction by methyl radicals from ethanethiol.

Fig. 8. Arrhenius plot for hydrogen-atom abstraction by methyl radicals from diethylhydroxylamine.

quently, our activation energy is much lower than the value estimated by Kerr and Trotman-Dickenson from their room temperature rate coefficient and assumed A factor. It is to be noted that the value determined in this work is more in accordance with the rate coefficient of the $CH_3 + H_2S$ reaction.

The Arrhenius plot of rate coefficients determined over the temperature range 298 - 430 K for the hydrogen-atom abstraction from diethylhydroxylamine by methyl radicals is presented in Fig. 8. Weighted least-squares fitting of the data yields

$$\log(k_{11}/dm^3 mol^{-1} s^{-1}) = \frac{(8.0 \pm 0.4) - (12.7 \pm 2.6)}{RT \ln 10} \text{ kJ mol}^{-1} \quad (22)$$

From eqn. (22) one calculates $k_{11} = 6.0 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for 298 K which is not inconsistent with the value of $3.0 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ given by Abuin *et al.* [11] for the analogous reaction of $C_2H_5 + (C_2H_5)_2NOH$.

Considering the Arrhenius parameters determined for the metathesis reactions of CH_3 with C_2H_5SH and $(C_2H_5)_2NOH$, one finds that both reactions have "normal" A factors and low activation energies. The latter are due to the weakly bound hydrogen atoms present in the substrates. The activation energies of the two reactions are similar (E_A for the C_2H_5SH reaction appears somewhat lower than that for the $(C_2H_5)_2NOH$ reaction). The greater reactivity of the thiol compound is surprising at first if one only takes into account the strengths of the $RS-H$ and R_2NO-H bonds. However, similar observations were made by Encina *et al.* [4] who explained the observed order of reactivity in terms of the repulsion between carbon and oxygen atoms being larger in the $CH_3 + (C_2H_5)_2NOH$ reaction than the repulsion between carbon and sulphur in the $CH_3 + H_2S$ and $CH_3 + RSH$ reactions.

On the basis of these results, one can state that both substances studied are reactive substrates with respect to hydrogen-atom abstraction by CH_3 ;

however, mainly as a result of the lower activation energy, ethanethiol is a more efficient free-radical scavenger.

3.3. Rate coefficient for acetone triplet state quenching by additives

Triplet acetone quenching by H_2S , $\text{C}_2\text{H}_5\text{SH}$ and $(\text{C}_2\text{H}_5)_2\text{S}$ has been studied by phosphorescence decay measurements carried out in the presence of sulphurous additives. The acetone concentration was $5.4 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1}$ and the additive concentration varied from 0 to $10^{-3} \text{ mol dm}^{-3}$ in the reaction series. The ${}^3\tau_0/{}^3\tau$ vs. QH plots for the three additives are given in Fig. 9. From the slopes of the Stern–Volmer plots, the quenching constants $k_{10}{}^3\tau_0$ are obtained which supply, by means of the triplet lifetime ${}^3\tau_0 = 1.95 \times 10^{-4} \text{ s}$, the rate coefficients of triplet state quenching given in Table 3.

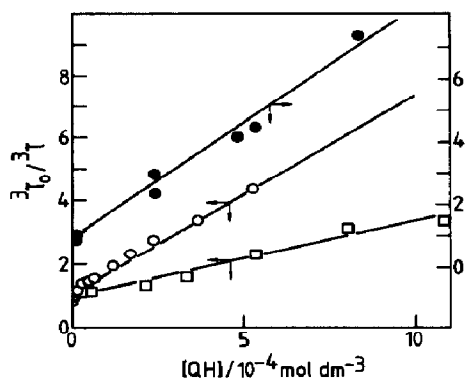


Fig. 9. Stern–Volmer plots for triplet-state quenching by sulphurous additives: ○, H_2S ; ●, $\text{C}_2\text{H}_5\text{SH}$; □, $(\text{C}_2\text{H}_5)_2\text{S}$.

TABLE 3

Rate coefficients for triplet state quenching by sulphurous compounds at room temperature

	Additive		
	H_2S	$\text{C}_2\text{H}_5\text{SH}$	$(\text{C}_2\text{H}_5)_2\text{S}$
$k_{10}{}^3\tau_0/10^3 \text{ dm}^3 \text{ mol}^{-1}$	6.4 ± 0.2	7.4 ± 0.8	2.5 ± 1.1
$k_{10}/10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	3.3 ± 0.1	3.8 ± 0.4	1.3 ± 0.6

It may be seen that the k_{10} values are all of the order of $10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, i.e. the rate of triplet state quenching by the sulphurous additives is much less than the diffusion-controlled rate.

Triplet acetone quenching by diethylhydroxylamine has been studied at 298 K using the same technique (phosphorescence decay measurements) as was applied in the case of the sulphurous compounds. The acetone concentration was $5.4 \times 10^{-3} \text{ mol dm}^{-3}$ and the $(\text{C}_2\text{H}_5)_2\text{NOH}$ concentration varied from 0 to $8 \times 10^{-6} \text{ mol dm}^{-3}$. From the Stern–Volmer plot of the

lifetime data, a quenching constant of $k_{10}{}^3\tau_0 = (4.9 \pm 0.25) \times 10^5 \text{ dm}^3 \text{ mol}^{-1}$ was derived and with our room temperature ${}^3\tau_0 = 1.95 \times 10^{-4} \text{ s}$ value a rate coefficient of $k_{10} = (2.5 \pm 0.13) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ was obtained for triplet-acetone quenching by diethylhydroxylamine.

Limited information on the temperature dependence of k_{10} can be obtained by using the quenching constants $k_{10}{}^3\tau_0$ derived from the quantum-yield measurements (given in Table 3) together with time-resolved phosphorescence measurement of ${}^3\tau_0$. The results given in Table 4 show that the rate coefficients for triplet quenching by diethylhydroxylamine are of the order of $10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and depend only slightly on temperature. The present results on acetone-triplet quenching by diethylhydroxylamine are in very good agreement with the results of Cáceres *et al.* [13] for the triplet-benzil-diethylhydroxylamine system and are somewhat higher but still in accordance with the quenching results published [4] for $(\text{C}_2\text{H}_5)_2\text{NOH}$ -triplet-ketone systems.

TABLE 4

Rate coefficients for triplet state quenching by diethylhydroxylamine

	Temperature (K)		
	298	323	353
$k_{10}{}^3\tau_0/10^4 \text{ mol dm}^{-3}$	49 ^a	19 ^b	6 ^b
${}^3\tau_0/10^{-4} \text{ s}$	1.95 ^a	1.23 ^c	0.25 ^a
$k_{10}/10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	2.5	1.6	2.4

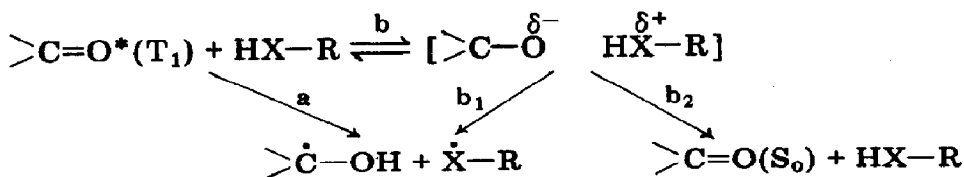
^aTime-resolved phosphorescence decay measurements.

^bQuantum yield data derived from results given in Table 3.

^cTaken from the results of Kaskan and Duncan [12].

Comparing our hydroxylamine and thiol results we find, however, that hydroxylamine derivatives are far more efficient triplet state quenchers than the sulphurous compounds investigated. The rate coefficients k_{10} appear to be about two orders of magnitude higher for the former additives than for the latter class of compounds. To find an explanation for this difference, one has to consider the mechanism of quenching of the carbonyl triplet state by various additives.

We assume that the additives used can interact with excited $n\pi^*$ triplets of carbonyl compounds by two major paths: (i) direct hydrogen-atom abstraction by the $n\pi^*$ triplet ketone from the substrate, *i.e.* a photoreduction reaction; (ii) charge transfer complex formation between the triplet state and the substrate molecule, as suggested by Cohen and coworkers for benzophenone-triplet quenching by amines [14] and thiols and thioethers [15], which is followed either by dissociation of the complex into ground state ketone and substrate molecules or by hydrogen shift resulting in the formation of the photoreduction products. The assumed quenching mechanism is presented in Scheme 2.



Scheme 2.

In this scheme $>C=O^*(T_1)$ is the excited triplet molecule and $R-XH$ represents the thiol or hydroxylamine quenching molecules.

It is suggested that high quenching efficiency of diethylhydroxylamine is caused by the fast consumption of the excited $n\pi^*$ triplet ketone both through direct photoreduction (reaction path a) and through charge transfer (path b). The low strength of the $(C_2H_5)_2NO-H$ bond and the relatively small repulsion between the carbonyl and hydroxylamine oxygen atoms during the approach of the molecules results in an efficient direct hydrogen-atom abstraction via path a. The photoreduction process gives a stabilized diethyl nitroxide radical. The same factors which are important in the case of direct photoreduction also favour hydrogen-atom abstraction via charge transfer complex formation, *i.e.* by path b_1 .

In case of sulphurous compounds, the conditions of triplet state quenching are less favourable than with hydroxylamines. The greater bond strengths and higher ionization potentials for thiols and thioethers make both direct hydrogen abstraction (path a) and quenching via a charge transfer complex (path b) slower. The mechanism of quenching probably also depends on the type of sulphurous compound.

3.4. Triplet-state quenching and free-radical scavenging efficiencies

Experimental observations described in the earlier sections indicate that diethylhydroxylamine is much more reactive than the thiols and thioethers towards $n\pi^*$ triplet carbonyls. However, the sulphurous compounds prove to be more effective free-radical trapping agents than the hydroxylamine derivatives. Quantitative kinetic data for triplet-quenching and metathesis reactions have been given above. In this section we propose two characteristic functions which may be used as simple and easily accessible measures of the free-radical trapping and triplet state quenching efficiencies of additives.

Free-radical scavenging can be best characterized by the rate of hydrogen-atom abstraction by the radical from a substrate. We propose as a measure of methyl-radical scavenging efficiency the following ratio of rates of formation of methyl-radical products:

$$\eta_H = \frac{R(CH_4)}{R(CH_4) + 2R(C_2H_6)} \quad (23)$$

The quantity η_H , as defined by eqn. (23), is an approximation of the true scavenging efficiency. Under favourable conditions η_H represents the ratio of the rate of the CH_3 -radical scavenging reaction (11) to the overall rate of CH_3 -radical consumption. Although these conditions are often not entirely

fulfilled, the quantity given by eqn. (23) is generally a useful measure of the radical-scavenging efficiency under specified experimental conditions.

Triplet-quenching efficiencies may be conveniently characterized by means of triplet state lifetimes which are, in most cases, easy to measure. Thus

$$\eta_Q = \frac{{}^3\tau_0 - {}^3\tau}{{}^3\tau_0} \quad (24)$$

where ${}^3\tau_0$ and ${}^3\tau$ are the triplet state lifetimes in the absence and presence of the triplet-quenching additives. It can be shown easily that the physical meaning of η_Q defined by eqn. (24) is the ratio of the rates of triplet reactions (including quenching).

Free-radical trapping efficiencies η_H and triplet-state quenching efficiencies η_Q are given in Figs. 10, 11 and 12 at 298 K, a concentration of $[\text{CH}_3\text{COCH}_3]_0 = 5.4 \times 10^{-3} \text{ mol dm}^{-3}$ and a light intensity of 5×10^{-9}

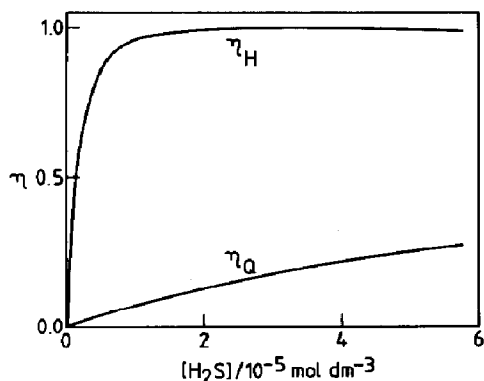


Fig. 10. Free-radical trapping efficiency η_H and triplet-state quenching efficiency η_Q of H_2S .

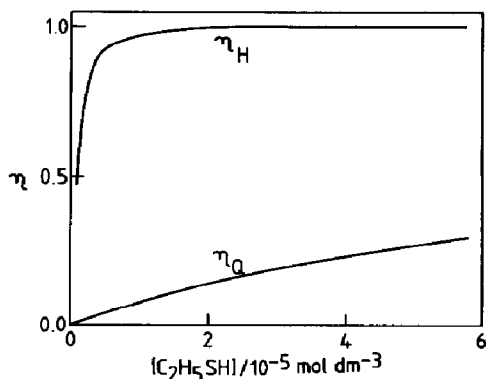


Fig. 11. Free-radical trapping efficiency η_H and triplet-state quenching efficiency η_Q of $\text{C}_2\text{H}_5\text{SH}$.

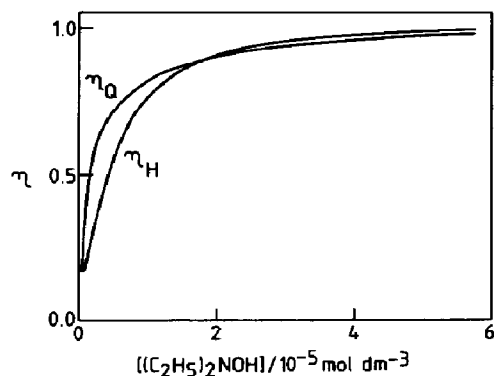


Fig. 12. Free-radical trapping efficiency η_H and triplet-state quenching efficiency η_Q of $(\text{C}_2\text{H}_5)_2\text{NOH}$.

einsteins $\text{dm}^{-3} \text{s}^{-1}$ as a function of H_2S , $\text{C}_2\text{H}_5\text{SH}$ and $(\text{C}_2\text{H}_5)_2\text{NOH}$ concentration. It is obvious from Figs. 10 and 11 that thiol-type additives are very efficient radical scavengers and inefficient triplet quenchers. Thus at $6 \times 10^{-6} \text{ mol dm}^{-3}$ thiol concentration about 95% of the free radicals are trapped ($\eta_{\text{H}} \geq 0.95$), while less than 5% triplet quenching is effected. The effect of hydroxylamines is, however, entirely different as seen from Fig. 12. At $6 \times 10^{-6} \text{ mol dm}^{-3}$ $(\text{C}_2\text{H}_5)_2\text{NOH}$ concentration about 65% radical trapping ($\eta_{\text{Q}} \approx 0.65$) and 75% triplet quenching ($\eta_{\text{Q}} \approx 0.75$) can be produced. The results indicate that there is no $(\text{C}_2\text{H}_5)_2\text{NOH}$ concentration at which either selective free-radical trapping or triplet quenching can be realized. Naturally, this conclusion applies only for compounds which have triplet state lifetimes similar to that of acetone.

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