Photochemistry of Hydroxyalkanones in Solution

Maria V. Encinas, Ana M. Rufs, and Eduardo A. Lissi *
Departamento de Química, Facultad de Ciencia, Universidad de Santiago de Chile, Santiago, Chile

The photochemistry of α-hydroxyketones (1,3-dihydroxyacetone, 3-hydroxybutan-2-one, 3-hydroxy-3-methylbutan-2-one, and 5-hydroxyoctan-4-one), β-hydroxyketones (4-hydroxy-3-methylbutan-2-one and 4-hydroxy-4-methylpentan-2-one), and a γ-hydroxyketone (5-hydroxypentan-2-one) has been studied by traditional steady-state photolysis and product analysis. Triplet yields were evaluated by *cis–trans* penta-1,3-diene isomerization, singlet lifetimes by absorption and fluorescence measurements, and triplet lifetimes from product-quenching experiments employing 1,3-dienes as selective triplet quenchers. α-Hydroxyketones photodecompose by a Type I cleavage, presumably from the excited triplet. β-Hydroxyketones decompose by –O–H intramolecular hydrogen abstraction and subsequent reactions of the produced biradicals, both from the excited singlet and triplet states. 5-Hydroxypentan-2-one gives Type II products from the singlet state, but no acetone is produced from the excited triplet.

Contrary to the wealth of information regarding the photochemistry of unsubstituted aliphatic ketones,[1,2] there exist few data regarding the photobehaviour of substituted compounds. In particular, with regard to aliphatic hydroxyketones, Baum *et al.*[3] have carried out a comprehensive analysis of the products obtained in the photolysis of 3-hydroxybutan-2-one, and 4-hydroxy-3-methylbutan-2-one, in both the gas and liquid phase. For the α-hydroxyketone, the results were explained in terms of two primary processes, an intramolecular rearrangement leading to acetaldehyde, and an α-bond cleavage leading to acetyl and α-hydroxyethyl radicals. The primary processes in the β-hydroxyketone were less well characterized, and it was concluded that in this ketone the triplet state did not appear to be photochemically important. Fischer *et al.*[4] have photolysed several aliphatic α-hydroxyketones, and carried out a CIDNP study of the secondary products that follow the α-cleavage. It was concluded that these ketones photoreact by breaking the carbonyl –C(OH) bond (Type I process) predominantly from the excited triplet state, but no estimate of the photocleavage rates was reported. Encinas *et al.*[5] have measured the efficiency of α-hydroxyketones as polymerization photoinitiators. From the high initiation yields obtained from 3-hydroxy-3-methylbutan-2-one and 3-hydroxybutan-2-one, it was concluded that most probably the free radicals arise from a very fast Type I photocleavage from the $n\pi^*$ excited triplet. In this respect, the effect of α-hydroxy substitution in aliphatic ketones would be similar to that reported for aromatic ketones.[6]

Taking into account the lack of quantitative kinetic data on the photochemistry of these ketones, and the fact that hydroxy and carbonyl groups are present in several biologically relevant compounds such as steroids and carbohydrates, we have carried out a study of the photochemistry of α-, β-, and γ-hydroxy-substituted alkanones.

Experimental

Photolyses were carried out on deaerated solutions at room temperature employing light of wavelength 313 nm from a medium-pressure mercury lamp. Product yields were measured by gas chromatography employing heptan-2-one in n-hexane [φ(acetone) 0.2] as actinometer.[7]

Type I cleavage products yields were determined in the presence of hexanethiol (in non-polar solvents) and cysteine (in aqueous solution) in order to trap quantitatively the free radicals produced.

Triplet yields were measured by the penta-1,3-diene *cis–trans* isomerization yield under conditions of total triplet quenching. Hexan-2-one in benzene (φ_T 0.38) was employed as reference.[8] When it was necessary, the results were corrected to take into account singlet quenching by dienes. The correction factor was obtained from fluorescence quenching experiments.

Singlet lifetimes were estimated from the fluorescence yield and the integrated absorption spectra. Butan-2-one (τ_S 2.1 ns in hexane[9]) was taken as reference. Fluorescence measurements were carried out on a Perkin-Elmer LS-5 spectrofluorimeter.

The hydroxyketones were K and K products. Other ketones employed were Fluka products of the highest purity available. All were purified by vacuum distillation and, when it was necessary, by preparative gas chromatography.

Spectroscopic-grade solvents (Merck; Uvasol) were used without further purification. *cis*-Penta-1,3-diene (Fluka) and 2,5-dimethylhexa-2,4-diene (Aldrich) were vacuum distilled prior to their use. 1,3-Dihydroxyacetone and 3-hydroxybutan-2-one solutions were prepared at least 24 h before use in order to attain monomer–dimer equilibration.

Results and Discussion

The present work comprises the photolysis of α-hydroxyketones (1)—(4), β-hydroxyketones (5) and (6), and a γ-hydroxyketone (7).

$HOCH_2COCH_2OH$
(1)

$CH_3COCH(OH)CH_3$
(2)

$CH_3COC(OH)(CH_3)_2$
(3)

$C_3H_7COCH(OH)CH_2CH_2CH_3$
(4)

$CH_3COCH(CH_3)CH_2OH$
(5)

$CH_3COCH_2C(OH)(CH_3)CH_3$
(6)

$CH_3COCH_2CH_2CH_2OH$
(7)

α-Hydroxyketones.—Compounds (1)—(3) do not have γ-hydrogens and they can only photoreact by a Norrish Type I bond cleavage or by hydrogen transfer from a five-atom-ring intermediate.[3] Ketone (1) is predominantly a monomer only in aqueous solution. In this solvent, the Type I photocleavage is almost quantitative for compounds (1) and (2). In the photolysis of (1) the methanol quantum yield is 0.9 ± 0.1 and, in the photolysis of (2), the acetaldehyde and ethanol yields were 1 ± 0.1. This last result implies that under our experimental

Table 1. Experimental data obtained in the photolysis of 5-hydroxyoctan-4-one in n-heptane.

$\varphi_{\text{n-butanol}}$	0.13 (Type I product)
$\varphi_{\text{n-butyraldehyde}}$	0.15 (Type I product)
$\varphi_{\text{propylene}}$	0.12 (Type II product)
$\varphi_{\text{propylene in the presence of 2,5-dimethylhexa-2,4-diene}}$	0.035 (Type II from the singlet)
φ_{triplet}	0.38
$(k_{\text{II}})_{\text{S}}$	6×10^8 s^{-1} [a]
β_{S}*	0.06 [b]
β_{T}*	0.33 [c]

[a] $(k_{\text{II}})_s$ taken as equal to $(1 - \varphi_{\text{T}})/\delta_{\text{S}}$. [b] β_{S} obtained from $(\varphi_{\text{II}})_{\text{S}}/(1 - \varphi_{\text{T}})$. [c] β_{T} obtained from $(\varphi_{\text{II}})_{\text{T}}/(\varphi_{\text{T}} - \varphi_{\text{I}})$.
* β_{T} and β_{T} are the fractions of biradicals giving Type-II products.

conditions the intramolecular decomposition of ketone (**2**) to acetaldehyde is negligible. This result contrasts with a previous report regarding the photolysis of this compound both in the gas phase and in non-protic solvents.[3] In these solvents, it was proposed that an intramolecular hydrogen bridge favours acetaldehyde formation. In aqueous solution reduced intramolecular bridging can be expected leading to a normal photodecomposition through α-bond cleavage.

The photochemistry of (**3**) in heptane can also be interpreted in terms of a simple Type I photocleavage since propan-2-ol (φ 0.95 ± 0.1) is produced almost quantitatively.

α-Hydroxyketones show a fluorescence band similar to that of unsubstituted ketones. Under conditions of equal absorbance, the fluorescence intensity of α-hydroxy-substituted ketones in water solution is considerably higher than those of the corresponding unsubstituted compound: $\varphi^{\text{Fl}}_{(1)}/\varphi^{\text{Fl}}_{\text{acetone}}$ 4.5; $\varphi^{\text{Fl}}_{(2)}/\varphi^{\text{Fl}}_{\text{butan-2-one}}$ 2; $\varphi^{\text{Fl}}_{(3)}/\varphi^{\text{Fl}}_{\text{3-methylbutan-2-one}}$ 2.

Since the extinction coefficients of the α-hydroxyketones are less than *ca.* 1.4 times those of the unsubstituted compounds, the above mentioned differences would imply larger singlet lifetimes, and hence lower rates of intersystem crossing. In this regard, α-hydroxy substitution would have an effect similar to that of α-methyl substitution.[10]

For ketones (**1**)—(**3**) it is difficult to obtain, from selective quenching experiments, the triplet lifetime, the triplet yield, and the proportion of products arising from the excited singlet. This difficulty is due both to the short triplet lifetime (as evidenced by the lack of thiol effect upon the product yield at concentrations up to 0.5M) and to the difficulty in finding a selective triplet quencher that does not interfere with the excited singlet and/or the produced radicals. Nevertheless, the almost quantitative cleavage observed, and the rather large singlet lifetime suggested by the fluorescence yields, would favour a photocleavage mechanism dominated by triplet processes. Similar conclusions have been previously reached from photopolymerization experiments[5] and from the triplet character of the geminal radical pair.[4] Nevertheless, it must be stated that some care must be exercised in relating the multiplicity of the free-radical pair to the multiplicity of the excited precursor.[11]

5-Hydroxyoctan-4-one can react by both Type I and II mechanisms, and quenching of Type II products could be, in principle, employed to monitor the triplet lifetime. The relevant data obtained employing this ketone (n-heptane as solvent) are summarized in Tables 1 and 2.

The singlet intramolecular hydrogen-abstraction rate given in Table 1 is almost a factor of two slower than that measured for unsubstituted alkyl ketones bearing secondary γ-hydrogens (*ca.* 6×10^8 s^{-1} per γ-hydrogen).[1] This reduced reactivity of the oxo group can be explained in terms of protection of the carbonyl group by formation of an intramolecular hydrogen bridge.

Table 2. K_{sv} slopes for 5-hydroxyoctan-4-one in n-heptane

Quencher	K_{sv}/l mol^{-1}
2,5-Dimethylhexa-2,4-diene	80
Isoprene	1 400
Penta-1,3-diene	1 700
Hexane-1-thiol	6 500

Table 3. Data obtained in the photolysis of 4-hydroxy-3-methylbutan-2-one in butyronitrile

$\varphi_{\text{acetaldehyde}}$	(Type I product)
$\varphi_{\text{n-propanol}}$	0.25 (Type I product)
$\varphi_{\text{butan-2-one}}$	0.06 (Type II product)
$\varphi_{\text{butan-2-one in the presence of 2,5-dimethylhexa-2,4-diene}}$	0.032 (Type II from the singlet)
φ_{T}	0.4
τ_{S}	1.8 ns
β_{S}	0.053
β_{T}	0.19
$(k_{\text{II}})_{\text{S}}$	3.3×10^8 s^{-1}
K_{sv}	32 l mol^{-1} [a]
τ_{T}	4 ns [b]
$(k_{\text{II}})_{\text{T}}$	1×10^8 s^{-1}
$(k_{\text{I}})_{\text{T}}$	1.6×10^8 s^{-1}

[a] Value obtained from 2,5-dimethylhexa-2,4-diene. Similar slopes were obtained from other diffusional quenchers. [b] Calculated from K_{sv} and taking k_{q} 8×10^9 l mol^{-1} s^{-1}.

The data of Table 2 were gathered to obtain the triplet lifetime. Nevertheless, the fact that the values obtained for several quenchers that usually react at the diffusionally controlled rate differ by more than a factor of 200, and that hexanethiol quenches the Type II products nearly 10^3 times more efficiently than 2,5-dimethylhexa-2,4-diene, would imply that the triplet is not the trapped species. Since, at the quencher concentrations employed, singlet quenching (as monitored by fluorescence measurements) is not significant, the data of Table 2 would imply that the species trapped is the 1,4-biradical. Trapping of triplet 1,4-biradicals by thiols has been previously reported,[12] but the K_{sv} values obtained were considerably smaller than those given in Table 2. There are no reported data on the trapping of 1,4-biradicals by olefins, but data obtained from aliphatic[5] and aromatic[13] ketones as photoinitiators of vinyl free-radical polymerization have been interpreted in terms of biradical monomer reactions. The data in Table 2, although not incompatible with previous observations, appear as anomalous due to the large K_{sv} values obtained. These data require, then, a particularly large lifetime of the α-hydroxy-substituted biradicals and/or a larger reactivity towards thiols and olefins. The lifetime of the biradical will be determined, among other factors, by the relative energies of the singlet and triplet species.[14] The singlet–triplet splitting is extremely sensitive to the average distance between both radical centres. The presence of two hydroxy groups introduces the possibility of an intramolecular hydrogen bridge, leading to significant changes in the biradical geometry. These changes could be reflected in the biradical lifetime. Nevertheless the β-values of both the singlet and triplet biradicals are similar to those reported for α-methyl-substituted alkanones of similar size.[1]

The K_{sv} slope obtained with 2,5-dimethylhexa-2,4-diene allows the estimation of an upper limit to the excited triplet lifetime. If it is assumed that diene triplet quenching is diffusionally controlled, we can estimate a triplet lifetime equal to (or shorter than) 10 ns. From this value $(k_{\text{II}})_{\text{T}} \geq 6.3 \times 10^7$ s^{-1} and $(k_{\text{I}})_{\text{T}} \geq 4 \times 10^7$ s^{-1}.

The limit obtained for the Type I photocleavage implies that,

Table 4. Data obtained in the photolysis of 4-hydroxy-4-methylpentan-2-one in n-heptane

φ_{acetone}	0.32
$\varphi_{\text{acetone in the presence of 2,5-dimethylhexa-2,4-diene}}$	0.08
φ_T	0.54
β_S	0.09[a]
β_T	0.22[a]
$(k_{II})_S$	6.5×10^8 s^{-1} (1.1×10^8)[c]
τ_T	0.32 ns[b]
$(k_{II})_T$	3×10^7 s^{-1} (0.8×10^7)[c]

[a] Evaluated by taking into account that two acetone molecules are produced by each C–C bond cleavage of the produced biradical. [b] From K_{sv} employing 2,5-dimethylhexa-2,4-diene. [c] Values obtained in the photolysis of 4-methylpentan-2-one.[1]

as in aromatic ketones,[6] α-hydroxy-substitution produces a remarkable increase in the rate of α-carbon cleavage.

This α-hydroxy effect is also compatible with the fact that no n-propane production was detected under our experimental conditions. The above considerations lead to $(k_I)_T/(k_{II})_T = 0.63$.

For ketones bearing secondary γ-hydrogens and with α-methyl substitution, the ratio of rate constants is *ca.* 0.43.[1] The effect of α-hydroxy substitution would lead to photochemistry similar to that of α-methyl substitution but with a major contribution from Type I photocleavage.

β-Hydroxyketones.—The relevant data obtained in the photolysis of ketones **(5)** and **(6)** are given in Tables 3 and 4.

The data of Table 3 show that ketone **(5)** photodecomposes by both a Type I cleavage and by Type II intramolecular hydrogen abstraction from the hydroxylic hydrogen.

$$\begin{aligned}
\mathrm{MeCOCH(Me)CH_2OH} &\xrightarrow{k_I} \mathrm{MeCO^{\bullet} + Me\dot{C}(H)CH_2OH} \\
&\xrightarrow{\mathrm{RSH}} \mathrm{MeCHO + Pr^nOH} \qquad (1) \\
&\xrightarrow{k_{II}} \mathrm{Me\dot{C}(OH)CH(Me)C(H_2)\dot{O}}
\end{aligned}$$

$$\begin{aligned}
\mathrm{Me\dot{C}(OH)CH(Me)C(H_2)\dot{O}} &\longrightarrow \beta\mathrm{(CH_2O + MeCOPr^n)} \qquad (2) \\
&\longrightarrow \text{Products} \qquad (3) \\
&\longrightarrow \mathrm{MeCOCH(Me)CH_2OH} \qquad (4)
\end{aligned}$$

The β-values of the alkylalkoxyl 1,4-biradicals are not significantly different from those for 1,4-biradicals produced by intramolecular γ-hydrogen abstraction in α-methyl-substituted alkanones.[1] Similarly, the $(k_I)_T$ value obtained by assuming that all the Type I products arise from the excited triplet is similar to other values reported for α-methyl-substituted alkanones.[1]

The $(k_{II})_T$ and $(k_{II})_S$ values deserve some comments since they imply hydrogen abstraction from a hydroxy bond. These values are quite similar to those measured for a secondary hydrogen abstraction in hexan-2-one in acetonitrile (4×10^8 and 1.2×10^8 s^{-1} for singlet[15] and triplet* states respectively), in spite of the O–H bond being considerably stronger than a secondary C–H bond.[16] Nevertheless, it has to be considered that alkoxyl radicals (a frequently mentioned model for $n\pi^*$ triplets) react with O–H bonds at a rate similar to that measured for CH_2 groups.[17] Semi-empirical calculations have provided a rationale for the particular reactivity of alkoxyl radicals towards O–H bonds.[18]

The data of Table 4 show that compound **(6)** decomposes by a Type II mechanism, since no Type I products (acetaldehyde or t-butyl alcohol) were detected. In this ketone, both –C–H or –O–H γ-hydrogen abstraction can explain acetone formation by bond cleavage of the corresponding 1,4-biradicals. Nevertheless, the fact that both $(k_{II})_S$ and $(k_{II})_T$ are considerably larger than those measured for 4-methylpentan-2-one[1] would favour abstraction of the hydroxylic hydrogen. The $(k_{II})_T$ value is smaller than that found for ketone **(5)**, but the difference can be due mostly to the different polarities of the solvents employed.[1] The lower β-values obtained for ketone **(6)** than that for ketone **(5)**, in particular β_S, are compatible with the known effect of α-methyl substitution upon biradical behaviour.[1]

Table 5. Data obtained in the photolysis of 5-hydroxypentan-2-one in butyronitrile solution

φ_{acetone}	0.1
$\varphi_{\text{acetaldehyde}}$	0.097
$\varphi_{\text{acetone in the presence of 0.8M 2,5-dimethylhexa-2,4-diene}}$	0.1
τ_S	0.6 ns
φ_T	0.5
$(k_{II})_S$	8.3×10^8 s^{-1}
β_S	0.21
β_T	<0.05[a]
τ_T	3.2 ns[b]
$(k_{II})_T$	3×10^8 s^{-1}[a]

[a] Obtained assuming that the triplet disappears by intramolecular hydrogen abstraction. [b] From penta-1,3-diene *cis–trans* isomerization as a function of *cis*-concentration.

γ-Hydroxyketones.—Data obtained in the photolysis of ketone **(7)** are given in Table 5.

The detected products are those expected from a Type II photoreaction. Nevertheless, the facts that 2,5-dimethylhexa-2,4-diene up to 0.8M does not alter the acetone or acetaldehyde quantum yields, while at lower concentrations significant *cis*- to *trans*-penta-1,3-diene isomerization is observed, imply that the acetone is produced almost exclusively from the singlet state. The value of $(k_{II})_S$ is very close to that measured for hexan-2-one (8.7×10^8 s^{-1})[15] while β_S is considerably larger than that reported for this compound (β_S in hexan-2-one = 0.13).

The lack of acetone production from the excited triplet is most unexpected. This result must imply another reaction from the triplet than γ-hydrogen abstraction, or a very low β_T. With regard to this last possibility, it has to be mentioned that the corresponding aromatic 1,4-biradical $[C_6H_5\dot{C}(OH)CH_2CH_2\dot{C}HOH]$ gives acetophenone with β_T 0.25.[19] With regard to the first possibility, the only possible alternative pathway could be intramolecular transference from the O–H bond. Intramolecular hydrogen abstraction through seven-membered rings has been proposed in several systems[20] and evaluated by semi-empirical calculations.[21] This abstraction is slower than normal γ-abstraction through a six-atom complex due to greater entropy loss, but the peculiar reactivity of the O–H bonds (see β-hydroxyketones) could make up the difference. From the triplet lifetime we can infer that the triplet decay takes place with a rate constant of 3×10^8 s^{-1}. The fact that this value is larger than that measured for **(5)** (see Table 3) would suggest that γ-hydrogen abstraction from the O–H bond is not the main decay path of the excited triplet. In agreement with this conclusion, 4-hydroxypentanal, one of the expected products from the 1,5-biradical, was not detected under our

---

* Value measured from the Stern–Volmer plot employing *cis*-penta-1,3-diene as quencher in acetonitrile.

experimental conditions. We can thus conclude that the lack of acetone formation from the triplet is still an unresolved point.

Acknowledgements

Thanks are given to DICYT, University of Santiago, Chile, for financial support.

References

1 M. V. Encinas and E. A. Lissi, *J. Photochem.*, 1978, **8**, 131.

2 J. C. Scaiano, E. A. Lissi, and M. V. Encinas, *Rev. Chem. Intermed.*, 1978, **2**, 139.

3 E. J. Baum, L. D. Hess, J. R. Wyatt, and J. N. Pitts, *J. Am. Chem. Soc.*, 1969, **91**, 2461.

4 (*a*) B. Blank, A. Henne, G. P. Laroff, and H. Fischer, *Pure Appl. Chem.*, 1975, **41**, 475; (*b*) G. P. Larroff and H. Fischer, *Helv. Chim. Acta*, 1973, **56**, 2011.

5 M. V. Encinas, E. A. Lissi, V. Koch, and E. Elorza, *J. Polym. Sci., Polym. Chem. Ed.*, 1980, **20**, 73.

6 (*a*) J. Eichler, C. P. Herz, I. Naito, and W. Schnabel, *J. Photochem.*, 1980, **12**, 225; (*b*) F. D. Lewis, R. T. Lauterbach, H. G. Heine, W. Hartmann, and H. Rudolph, *J. Am. Chem. Soc.*, 1975, **97**, 1519.

7 F. G. Golemba and J. E. Guillet, *Macromolecules*, 1972, **5**, 63.

8 M. V. Encinas and E. A. Lissi, *J. Photochem.*, 1975, **4**, 321.

9 (*a*) N. C. Yang, M. H. Hui, D. M. Shold, N. J. Turro, R. R. Hautala, K. Dawes, and J. C. Dalton, *J. Am. Chem. Soc.*, 1977, **99**, 3023; (*b*) J. C. Dalton, M. W. Geiger and J. J. Snyder, *ibid.*, 1976, **98**, 398.

10 (*a*) M. O'Sullivan and A. C. Testa, *J. Am. Chem. Soc.*, 1970, **92**, 5842; (*b*) D. A. Hansen and E. K. C. Lee, *J. Chem. Phys.*, 1975, **62**, 183.

11 E. Abuin and E. A. Lissi, *J. Photochem.*, 1976—1977, **6**, 1.

12 (*a*) M. V. Encinas, P. J. Wagner, and J. C. Scaiano, *J. Am. Chem. Soc.*, 1980, **102**, 1357; (*b*) M. V. Encinas, E. A. Lissi, and H. Soto, *J. Photochem.*, 1981, **16**, 43.

13 J. C. Scaiano and M. Hamity, *J. Photochem.*, 1975, **4**, 229.

14 A. H. Goldberg and D. A. Dougherty, *J. Am. Chem. Soc.*, 1983, **105**, 284.

15 M. V. Encinas, E. A. Lissi, and J. C. Scaiano, *J. Phys. Chem.*, 1980, **84**, 948.

16 S. W. Benson, 'Thermochemical Kinetics', Wiley, New York, 1976.

17 D. Griller and K. U. Ingold, *J. Am. Chem. Soc.*, 1974, **96**, 630.

18 A. A. Zavitzas and A. A. Melikian, *J. Am. Chem. Soc.*, 1975, **97**, 2757.

19 P. J. Wagner and A. E. Kemppainen, *J. Am. Chem. Soc.*, 1972, **94**, 7495.

20 P. J. Wagner and R. G. Zepp, *J. Am. Chem. Soc.*, 1971, **93**, 4958.

21 C. M. Previtali and J. C. Scaiano, *J. Photochem.*, 1973—1974, **2**, 321.

Received 26th *June* 1984; *Paper* 4/1095