Photochemical Reactions of Aliphatic Aldehydes in Solution

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Simple aliphatic aldehydes with a C_4 or longer chain undergo ' type 2 ' photoelimination and photocyclisation as major reactions in solution. Both singlet and triplet $n\pi^*$ states are direct precursors to products in these reactions. Quenching studies show that the triplet lifetime, governed largely by the rate constant for intramolecular hydrogenabstraction, varies with the substituent at position 4 in the chain.

THE 'type 2' photoelimination for aliphatic and aromatic ketones is well documented, and the mechanism of reaction has been elucidated in some detail.¹ For aliphatic ketones in solution the reaction occurs from both the first excited singlet state and the first excited triplet state.² In the triplet state reaction, a diradical intermediate (1) is involved, which can revert to the ground state starting ketone, undergo cleavage to the enol and alkene, or undergo ring-closure to give a cyclobutanol (see Scheme). A similar intermediate is



postulated ³ for the singlet state reaction. For aromatic ketones ArCO·CH₂·CH₂·CH₂R² only the triplet state is involved.4

There are reports of similar reactions for aliphatic aldehydes,⁵ aliphatic esters,⁶ esters of aromatic carboxylic acids,⁷ and other systems, but there are few quantitative rate data except for the aromatic esters. The present study of aliphatic aldehydes is intended to provide quantitative results in a system other than the intensively studied ketones.

Three primary chemical processes are postulated ⁸ for the excited states of aliphatic aldehydes: decarbonylation by a concerted mechanism (reaction 1); α -cleavage (reaction 2); and a process leading to products of

⁴ See F. D. Lewis and T. A. Hilliard, J. Amer. Chem. Soc., 1970, 92, 6672 and references therein.

 β -cleavage and cyclobutanol (reaction 3). The excited state precursor for reaction (3) has not been identified with certainty. In the vapour phase, a triplet state

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$$CH_2 CH_2 Me + CO$$
 (1)

$$(RCH_{2} \cdot CH_{2} \cdot CH_{2} \cdot CHO)^{*} \xrightarrow{} RCH_{2} \cdot CH_{2} \cdot CH_{2} + HCO \qquad (2)$$

$$RCH:CH_{2} + CH_{2} \cdot CHOH + \square_{R}^{OH} (3)$$

has been suggested for butanal,⁹ while in solution a singlet state has been suggested for several aliphatic aldehydes.10

RESULTS AND DISCUSSION

In the present study the simple aldehydes (2)—(6) were each irradiated in benzene or acetonitrile at 30 °C with a 300 nm source. The identified products were acetaldehyde (isolated by distillation and identified as the 2,4-dinitrophenylhydrazone), the alkene expected from β -cleavage (identified by retention time on g.l.c.), and the corresponding cyclobutanol (7)-(11). The cyclobutanols were isolated by preparative g.l.c., and the structures were assigned on the basis of spectral data. Of particular interest was the position of the C-1 proton signal in the n.m.r. spectra. For cyclobutanol (7) the signal is centred at τ 5.85, for (11) at 6.23. The spectra of (8)—(10) show two sets of signals for this proton, one at τ 5.7–5.8, and the other at *ca*. $6\cdot 3$ — $6\cdot 4$. The signal at lower field is tentatively

- * R. P. Borkowski and P. Ausloos, J. Amer. Chem. Soc., 1962, 84, 4044. ¹⁰ P. Borrell, J. Amer. Chem. Soc., 1964, 86, 3156.

¹ See J. C. Dalton and N. J. Turro, Ann. Rev. Phys. Chem.,

^{1970, 21, 499} and references therein. ² P. J. Wagner and G. S. Hammond, J. Amer. Chem. Soc., 1966, 88, 1245.

³ N. C. Yang, S. P. Elliott, and B. Kim, J. Amer. Chem. Soc., 1969, **91**, 7551.

⁵ E.g., R. E. Rebbert and P. Ausloos, J. Amer. Chem. Soc., 1967, **89**, 1573.

 ⁶ E. g., J. E. Gano, *Tetrahedron Letters*, 1969, 2549.
 ⁷ J. A. Barltrop and J. D. Coyle, *J. Chem. Soc.* (B), 1971, 251.
 ⁸ J. G. Calvert and J. N. Pitts, 'Photochemistry,' Wiley, View, Vie New York, 1966, p. 369.

assigned to the C-1 proton in the cis-isomer (12), and the signal at higher field to the C-1 proton in the transisomer (13).

Me $[CH_2]_n$ CHO (2) n = 2 (3) n = 3 (4) n = 4 (5) n = 5OH ,OH Me2CHCH2CH2CH2 -Me Мe (6)(10)(11) (7) (8) (9) OH (12) / ОН (13)

Quantitative estimation of the products in benzene solution was achieved by analytical g.l.c. with internal standards; correction factors being applied for each compound. The ratio of acetaldehyde to alkene was in all cases ca. 1.0:0.9-1.0, and the amounts of other products with short retention time were less than 10% (in some cases much less than 10%) of acetaldehyde. The ratios of cyclobutanols to acetaldehyde, and of cyclobutanol isomers are given in Table 1.

TABLE 1

Product ratios in benzene solution

Aldehyde	Cyclobutanols : Acetaldehyde	Ratio of cyclobutanols
(2)	0.39	
(3)	0.25	1.2
(4)	0.26	1.1
(5)	0.30	1.1
(6)	0.10	

The ratio of cyclisation to elimination varies according to the substitution pattern at C-4 of the aldehyde. The variation represents only a small change (<4 kJmol⁻¹) in the difference in activation energy for the two pathways from butanal to 4-methylpentanal, and may in any case be accounted for by the different ratio of singlet to triplet reaction along the series. The ratio of cyclobutanol isomers is near 1:1, which suggests that steric restriction in the transition states between the diradical and cyclobutanols is not greatly affected by the relative orientation of the groups on the two radical centres.

It was not possible to measure accurately the proportion of aldehyde consumed which is not accounted for by the elimination and cyclisation products, because the quantitative data were obtained from photolyses with low conversions only, and the errors involved in measuring the loss of starting material are large. There was a greater discrepancy (between aldehyde consumed and products formed) for butanal than for hexanal, and for hexanal than for 4-methylpentanal. This is reasonable if competing α -cleavage occurs to an

¹¹ P. Ausloos and R. E. Rebbert, J. Amer. Chem. Soc., 1964, 86, 4803.

appreciable extent, since the rate constant for α -cleavage should be unaffected by substitution at C-4, whereas the rate constant for intramolecular y-hydrogen abstraction should be considerably affected. That a-cleavage should be more important for aldehydes than for ketones is not indicated by the C(1)-C(2) bond strengths (ca. 330 kJ mol⁻¹ for acetaldehyde, 325 kJ mol⁻¹ for acetone) nor by the relative triplet energies (aldehydes quench the triplet state of acetone,¹¹ and presumably have a lower triplet energy). The observed importance of decarbonylated products for aldehydes in solution is probably accounted for by some concerted character in the decarbonylation process, as suggested by Schaffner ¹² and others.

The irradiation of 4-methylpentanal (6) was carried out in different solvents, and the relative quantum vields for formation of acetaldehyde and for loss of starting material were measured (Table 2). An order

TABLE 2	2
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Relative quantum yields for 4-methylpentanal in different solvents

Solvent $\phi (-4$ -methyl-	Benzene 1.00	Aceto- nitrile 1·24	Methanol 1·40	t-Butyl alcohol 1·31
ϕ (+ acetaldehyde)	0.85	0.74	0.39	1.07

of magnitude value for the absolute quantum yield was determined with valerophenone in acetonitrile as a secondary standard actinometer solution.¹³ This value was 0.69 for loss of 4-methylpentanal in benzene. In solvents with readily abstracted hydrogen atoms, notably methanol, additional products were formed. presumably as a result of effective competition by processes involving intermolecular hydrogen abstraction from solvent, but were not characterised.

Penta-1,3-diene (up to 3M) was employed as a triplet quenching probe to investigate the mechanism of reaction for aldehydes (2), (4), and (6). In each case it was found that part of the reaction was quenched efficiently and part was relatively unaffected. This indicates that reaction occurs to an appreciable extent from both a quenchable (long-lived triplet) and an unquenchable (singlet or short-lived triplet) state. These are probably the $n\pi^*$ triplet and $n\pi^*$ singlet states respectively. The experimental results, corrected for competitive light absorption by the acetaldehyde produced in the reaction, were used to construct linear quenching plots of $(\phi_0/\phi)_{\text{triplet}}$ against quencher concentration, where ϕ_0 is the quantum yield for a particular process in the absence of quencher, ϕ is the quantum yield in the presence of quencher, and the subscript indicates that reaction from the singlet state has been subtracted out '. The slopes of these linear plots are given in Table 3, and the triplet lifetime is calculated from the slope with a value of 5.0×10^9 l mol⁻¹ s⁻¹ for



K. Schaffner, Chimia (Switz.), 1965, 19, 575.
 P. J. Wagner, J. Amer. Chem. Soc., 1967, 89, 5898.

the bimolecular quenching rate constant in benzene.¹⁴ The absolute values of the triplet lifetimes and of rate constants calculated from these lifetimes depend on the exact value of the quenching rate constant, but the relative values and the general argument are not

TABLE 3

Kinetic data from triplet quenching experiments

Quenching slope (l mol ⁻¹) for appearance of				
Aldehyde	Acetaldehyde	Alkene	Cyclobutanol	(ns)
(2)	170	180	200	35
(4)	32	30	38	$6 \cdot 2$
(6)	6.8	7.0	6.7	1.4

^a Calculated using the average quenching slope for acetaldehyde and alkene.

affected unless the value is grossly in error by several orders of magnitude.

The triplet lifetimes decrease in the order butanal, hexanal, 4-methylpentanal, and this variation is best accounted for by a consideration of the pathways open to the quenchable triplet state, namely phosphorescence, radiationless decay, and intramolecular hydrogen abstraction. In the following scheme, S_0 represents the ground state of the aldehyde, T_1 the quenchable triplet state, and R the diradical produced by hydrogen abstraction from C-4. The triplet lifetime τ_T is given

$$T_1 \longrightarrow S_0 + h\nu \qquad (k_p)$$

$$T_{1} \longrightarrow S_{0} \qquad (k_{-T})$$
$$T_{1} \longrightarrow R \qquad (k_{R})$$

by $\tau_{\rm T}^{-1} = (k_{\rm p} + k_{\rm T} + k_{\rm R})$. The fact that $\tau_{\rm T}$ is markedly dependent on the nature of the 4-substituent indicates that $k_{\rm R}$ is the dominant term in this sum of rate constants, since it is the only term likely to increase markedly as the C-H bond at C-4 becomes progressively weaker in the order primary C-H, secondary C-H, tertiary C-H. The rate constant for phosphorescence in alkyl-substituted acetones is insensitive to changes in substitution at the α -position.¹⁵ Radiationless decay is retarded by alkyl substitution at this position,¹⁵ but this is an effect in the wrong direction to explain the present results. However, in view of the suggestion that the mechanism for radiationless decay involves energy dissipation via the bonds to the α -carbon atom, it is possible that substitution at the γ -position has little effect on this process. The conclusion is that the decrease in triplet lifetime across this series of aliphatic

¹⁴ P. J. Wagner and A. E. Kemppainen, J. Amer. Chem. Soc., 1968, **90**, 5898.

aldehydes probably reflects the increasing ease of hydrogen abstraction as the C-H bond broken in this reaction becomes progressively weaker.

It is reported ¹⁶ that conjugated dienes react with the excited states of aliphatic aldehydes, and oxetan products have been isolated in certain cases; the reaction is more efficient at high diene concentration. In the present study products with relatively long retention time were observed by g.l.c. at high diene concentration, but in no case was the loss of aldehyde actually accelerated as the diene concentration increased. However, the discrepancy was sufficiently large to prevent accurate determination of a quenching slope for disappearance of starting material.

EXPERIMENTAL

Aldehydes (2)—(5) were obtained commercially, purified by distillation, stabilised with 0.1% quinol, and dried (MgSO₄). 4-Methylpentanal was prepared from 1-bromo-3-methylbutane and ethyl orthoformate. All the aldehydes were carefully distilled under nitrogen immediately prior to use.

Irradiations were carried out in a Rayonet photochemical reactor (Southern New England Ultraviolet Co., model RPR-100) with merry-go-round attachment (MGR-100) and RPR-300 nm lamps. For quantitative runs the aldehyde concentrations were 0.1-0.2M, and saturated hydrocarbons were used as internal standards for g.l.c. The temperature was constant at *ca*. 30 °C. Reaction was carried to <5% conversion in most runs, and analytical g.l.c. was carried out on a column made up as 20% di-ndecyl phthalate on Embacel. Relative peak areas were measured by triangulation or with a Kent Chromalog 2 digital integrator.

Preparative g.l.c. was performed on a similar column. The major isomeric photoproducts (>99% pure by g.l.c.) each showed v_{max} . 3350 (O-H) and 950 and 960 cm⁻¹ (fourmembered ring); n.m.r.: cyclobutanol (7) τ 5.85 (1H) and 7.7—8.9 (7H, including signal at 8.1 reduced in intensity by D₂O); 2-methylcyclobutanol (8) τ 5.78 and 6.41 (1H, both q, J 6.9—7.0 Hz) 7.3—7.4br (1H, reduced in intensity by D₂O), 7.5—9.1 (5H), and 9.13 (3H, d, J 6.7 Hz); 2-ethylcyclobutanol (9) τ 5.71 and 6.30 (1H, q, J 6.9 Hz), 6.63br (1H, reduced in intensity by D₂O), 7.5—9.0 (7H), and 9.13 (3H, t, J 7.0 Hz); 2-n-propylcyclobutanol (10) τ 5.71 and 6.31 (1H, m, J 6.8 Hz), 7.3br (1H, reduced in intensity by D₂O), and 7.5—9.2 (9H, including t, J 7.0 Hz, Me); 2,2-dimethylcyclobutanol (11) τ 6.23 (1H, t, J 7 Hz), 7.6—8.9 (5H, including signal at 8.1 reduced in intensity by D₂O), and 8.96 (6H, s).

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¹⁵ M. O'Sullivan and A. C. Testa, J. Amer. Chem. Soc., 1970, 92, 258.

¹⁶ N. C. Yang and W. Eisenhardt, J. Amer. Chem. Soc., 1971, 93, 1277.