Electron Spin Resonance of Transient Radicals During Photoreactions of Aliphatic Ketones

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Summary During u.v.-irradiation of aliphatic ketones in solution, e.s.r. spectra are observed of radicals due to photoreduction, Norrish Type I cleavage, and other reactions of excited ketones.

WE report an e.s.r. study on photoreactions of aliphatic ketones in methylcyclopentane and trichlorofluoromethane. The solutions (10% ketone v/v) were irradiated in the cavity of an e.s.r. spectrometer as they slowly flowed (0·05 ml/min) through a flat quartz cell, the temperature of which could be varied ($-110\ ^\circ C < T < +70\ ^\circ C$) by a flow of gaseous nitrogen. Filtered light (230 nm $< \lambda <$ 340 nm) from a 1 kW high-pressure mercury arc lamp (Philips SP 1000 W) was used.

During irradiation of acetone, ethyl methyl ketone, and methyl propyl ketone in methylcyclopentane, e.s.r. spectra of radicals produced in photoreductions[1-3] $Me_2\dot{C}OH$, $EtMe\dot{C}OH$, and $PrMe\dot{C}OH$ were observed. In all cases further lines were present, part of which (quartet of quintets) are attributed to the solvent radical $\underline{CH_2\cdot[CH_2]_3\cdot\dot{C}}\cdot Me$.

Isopropyl methyl ketone, methyl t-butyl ketone, and benzyl methyl ketone in methylcyclopentane gave intense and well resolved e.s.r. spectra of the radicals $Me_2\dot{C}H$, $Me_3\dot{C}$, and $Ph\dot{C}H_2$, respectively, which are formed by Norrish Type I cleavage of the excited ketones.[1-3] The lines of the radicals $Me\dot{C}(OH)COMe$[4] were also present in all three spectra. Acetyl radicals or photoreduction intermediates of the ketones were not observed. $Me_2\dot{C}H$ was found also during photolysis of di-isopropyl ketone in the same solvent. The Figure shows the spectrum of $Me_2\dot{C}H$ (A) and the $Me_3C\bullet$ lines (B) from di-isopropyl ketone and methyl t-butyl ketone, respectively at $-70\ ^\circ C$. Second order splittings are nearly fully resolved.

Irradiation of acetone, ethyl methyl ketone, and methyl propyl ketone in CCl_3F gave rather complex e.s.r. spectra from which $\bullet CCl_2F$ could be identified in all three cases. Other lines were in part due to $\bullet CH_2\bullet COMe$, $Me\dot{C}HCOMe$, and $Et\dot{C}HCOMe$, respectively.

Photolysis of pure CCl_3F yielded no e.s.r. spectrum. Therefore under our conditions the $\bullet CCl_2F$ radicals cannot be formed in appreciable amounts by direct photolysis of CCl_3F to give $\bullet Cl$ and $\bullet CCl_2F$. It is known, however,[5,6] that CCl_4 cleaves into $\bullet Cl$ and $\bullet CCl_3$ *via* exciplex formation with

TABLE

Coupling constants and g-factors

Radicals from reduction

Radicals	T/°C	Coupling constants (to ±0·05 G) $a_H(\beta)$	$a_H(\gamma)$	a_H(OH)	g ±0·0001	Ref.
$Me_2\dot{C}OH$	−13	19·46 (CH_3)			2·0031	8
$EtMe\dot{C}OH$	−13	19·50 (CH_3) 17·11 (CH_2)	0·35 (CH_3)	0·35	2·0031	
$PrMe\dot{C}OH$	−43	19·70 (CH_3) 16·38 (CH_2)	0·78 (CH_2)		2·0031	
$\underline{CH_2\cdot[CH_2]_3\cdot\dot{C}}\cdot Me$	−13	22·22 (CH_3) 32·87 (CH_2)			2·0027	

Radicals from Norrish Type I cleavage

Radicals	T/°C	Coupling constants (to ±0·02 G) $a_H(\alpha)$	$a_H(\beta)$	a_H(PL)	g ±0·0001	Ref.
$Me_2\dot{C}H$	−70	21·94	24·69		2·0026	9—11
$Me_3\dot{C}$	−70		22·74		2·0026	9—11
$Ph\dot{C}H_2$	+30	16·28		5·15 (*o*) 1·79 (*m*) 6·17 (*p*)	2·0026	10

Radicals formed in CCl_3F

Radicals	T/°C	Coupling constants (to ±0·1 G) $a_H(\alpha)$	$a_H(\beta)$	a_H(COMe)	g ±0·0001	Ref.
$\cdot CH_2COMe$	−80	19·7			2·0044	8
$Me\dot{C}HCOMe$	−30	19·0	22·2	0·9	2·0043	12
$Et\dot{C}HCOMe$	− 4	18·8	19·9	0·9	2·0043	
$\cdot CCl_2F$	−80	$a(^{35}Cl) = 10·4$ $a(^{37}Cl) = 8·7$	$a(F) = 84·0$		2·0069	13

excited molecules. We presume therefore that in solutions containing ketones CCl_3F can fragment in a similar process. The radicals $R\dot{C}HCOMe$ are probably then formed *via* reaction (1). This agrees with studies on the photolysis of

$$RCH_2COMe + \cdot Cl \longrightarrow R\dot{C}HCOMe + HCl \qquad (1)$$

gaseous mixtures of diethyl ketone and carbon tetrachloride[7] in which •Cl and not $\cdot CCl_3$ radicals were found to undergo reaction (1).

Coupling constants and g-factors of the observed radicals are summarized in the Table.

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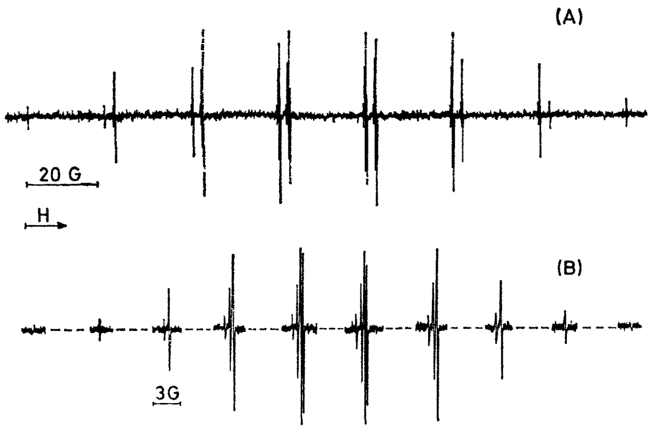

FIGURE. *E.s.r. spectrum of* $Me_2\dot{C}H$ (A) *and e.s.r. lines of* $Me_3\dot{C}$ (B) *at* −70°C.

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