

PHOTOLYSIS OF ALIPHATIC CARBOXYLIC ACIDS IN THE PRESENCE OF HYDROGEN-ATOM DONORS

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Recently, we used t-nitrosobutane (I) to trap radical intermediates in the photo-reduction of benzophenone by various hydrogen donors.¹ Analysis of the electron spin resonance (ESR) spectra of the nitroxides (II) thus formed (Eqn 1) enables one to deduce the nature of the



trapped radicals (see Ref. 1 and leading references therein). We have now studied the photolysis of aliphatic carboxylic acids, *viz.* acetic, propionic, butyric and hexanoic, in the presence of hydrogen donors and the same radical scavenger (I), and present evidence to indicate hydrogen abstraction from these donors. Typical parameters of the nitroxide radicals detected and the nature of the radical trapped in each case are summarized in Table I. The wavelengths of irradiation were in the region 230-250 nm (Bausch and Lomb High Intensity grating monochromator or JASCO CRM-FA Spectro-irradiator) where the proportion of radiation absorbed by the scavenger (in monomeric form) was small. "Blank" photolyses of the hydrogen-donor-scavenger solution (with the exception of ethers) did not give rise to nitroxide formation under the conditions used. Solutions were *ca* 2 M in the acid and 0.01 M in the scavenger and deoxygenated by outgassing with nitrogen before irradiation.

Using ethanol as hydrogen donor photolysis of all the acids gave rise to an ESR spectrum (a triplet of doublets, see Fig. 1a) indicating the trapping of radicals formed by abstraction of an α -proton of the ethanol. These signals were similar to those obtained previously¹ for the alcohol derived radical formed during photoreduction of benzophenone in this solvent. Examination of an ethanol solution of acetic acid after photolysis without the scavenger (by g.l.c. on Carbowax 1500) showed the formation of acetaldehyde (quantum yield of formation *ca* 0.01) which presumably arises from the alcohol-derived radical.

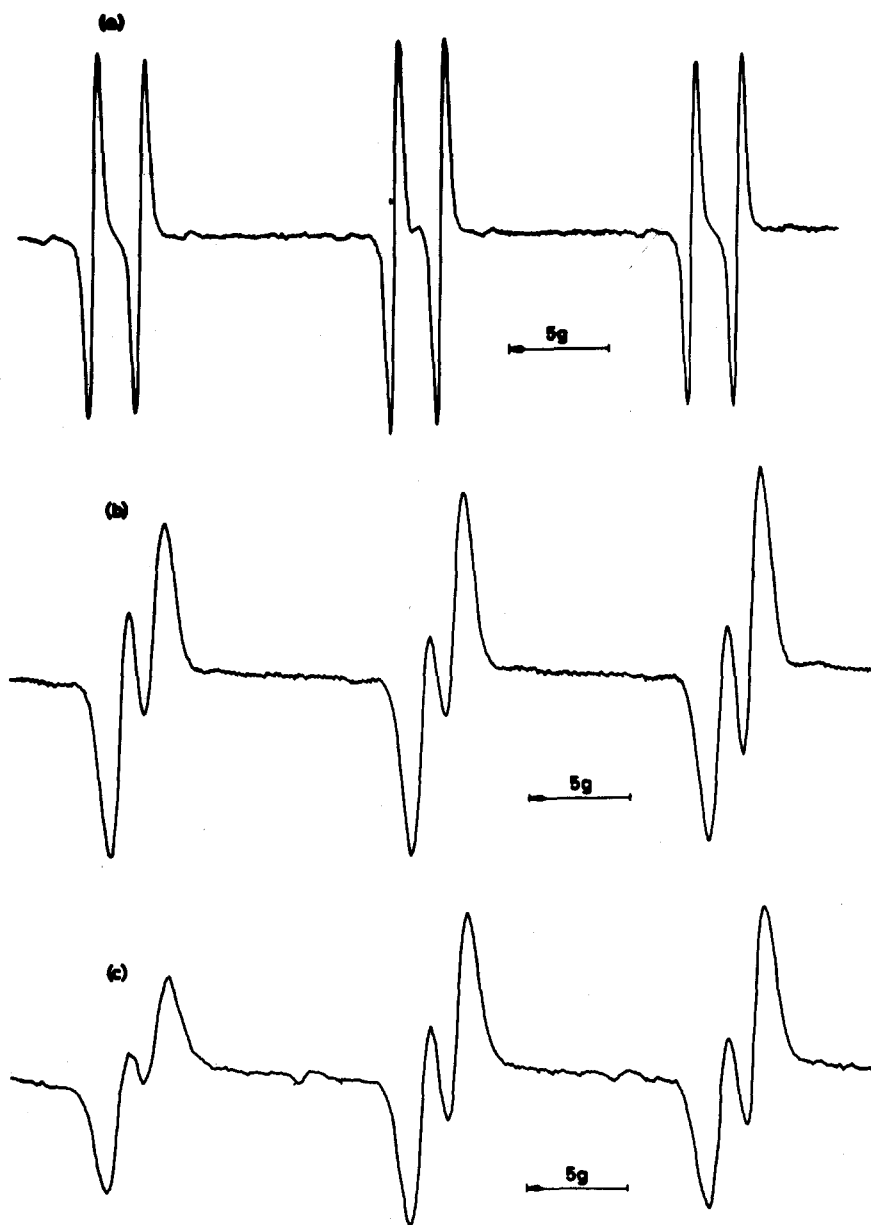


Fig.1. ESR spectra of nitroxide radicals formed during photolysis of aliphatic acid solutions containing *i*-nitrosobutane.
(a) acetic acid in ethanol, (b) acetic acid in *n*-heptane, (c) neat hexanoic acid.

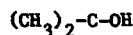
TABLE I

Nitroxide Radicals Formed During Photolysis of Aliphatic Acids in Various Solvents Containing
t-Nitrosobutane

Acid	Solvent	Trapped Radical	Hfs Constants (Gauss)	
$\text{CH}_3\cdot\text{COOH}$	$\text{CH}_3\cdot\text{CH}_2\text{OH}$	$\text{CH}_3\cdot\dot{\text{C}}\text{HOH}$	$a_N = 14.98,$	$a_H^{\text{CH}} = 2.31$
$\text{CH}_3\cdot\text{COOH}$	CH_3OH	$\dot{\text{C}}\text{H}_2\text{OH}$	$a_N = 14.88,$	$a_H^{\text{CH}_2} = 5.18$
$\text{CH}_3\cdot\text{COOH}$	$(\text{CH}_3)_2\cdot\text{CHOH}$	$\cdot\text{H}^*$	$a_N = 13.80$	$a_H = 12.88$
$\text{CH}_3\cdot\text{COOH}$	$\text{CH}_3\cdot(\text{CH}_2)_5\cdot\text{CH}_3$	$\text{CH}_3\cdot(\text{CH}_2)_n\cdot\dot{\text{C}}\text{H}\cdot(\text{CH}_2)_{4-n}\cdot\text{CH}_3$	$a_N = 14.88,$	$a_H^{\text{CH}} = 1.50$
$\text{CH}_3\cdot\text{COOH}$	$\text{CH}_3\cdot\text{CH}_2\text{OCH}_2\cdot\text{CH}_3$	$\text{CH}_3\cdot\dot{\text{C}}\text{HOCH}_2\cdot\text{CH}_3$	$a_N = 13.97,$	$a_H^{\text{CH}} = 2.74$
$\text{CH}_3\cdot(\text{CH}_2)_4\cdot\text{COOH}$	-	$\text{CH}_3\cdot(\text{CH}_2)_n\cdot\dot{\text{C}}\text{H}\cdot(\text{CH}_2)_{3-n}\cdot\text{COOH}$	$a_N = 14.88,$	$a_H^{\text{CH}} = 1.50$

* See text.

With methanol as hydrogen donor the nitrogen hyperfine component of the nitroxide signal was split into a triplet, again indicating abstraction of an α -proton from the alcohol. However, with isopropanol only a transient signal (triplet of doublets) was observed and we believe this to be due to t-butyl nitroxide formed by abstraction of a proton by the t-nitroso-butane scavenger from one of the radicals present (e.g. III).



III

When aliphatic hydrocarbons, e.g. n-heptane, were used the nitrogen hyperfine component was split into a broad doublet (see Fig. 1b) which was similar to that observed in the benzophenone system.¹ This broadening of the doublet may be attributed to hydrogen abstraction from more than one site in the heptane molecule. It is of interest that the ease of hydrogen abstraction, judged by the intensity of the nitroxide signal observed, was acetic > propionic \approx butyric > hexanoic acid.

The situation with ether, e.g. diethyl ether, was less clear cut; the scavenger absorbs more of the incident radiation because of a red spectral shift in this solvent. However, a spectrum (triplet of doublets) similar to that observed in the benzophenone system¹ was obtained.

Irradiation of neat hexanoic acid and the scavenger gave a signal similar to, but not identical with, that obtained in n-heptane solution. This could indicate that abstraction of a proton from the hydrocarbon chain occurs but it is not possible to say whether the process is inter- or intra-molecular. Neat butyric acid gave rise to a weak signal (a triplet of doublets) whereas acetic acid yielded no signal at all.

Very little is known about the hydrogen-abstracting properties of the excited carboxylic acid chromophore although Norrish Type II splits are well established for aliphatic esters² and one acid, butyric.³ Further work is needed to elucidate the mechanism of formation of the radicals trapped in the present studies and it is hoped that this Note will stimulate research on the photolysis of aliphatic carboxylic acids in solution.

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