Detection and Identification of Organic Radicals Produced in the Low Pressure Silent Electric Discharge by an Electron Spin Resonance Spin Trapping Technique

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A method is described whereby free radicals are produced in a low pressure silent electric discharge between glass surfaces and are simultaneously deposited with 2-methyl-2-nitrosopropane as a spin trap on a cold surface. The resulting deposit is warmed to room temperature and subjected to electron spin resonance examination. A variety of alkyl and other radicals were trapped with different reactants in the discharge tube.

The technique of electron spin resonance spin trapping has recently been developed to detect and identify organic free radicals in solution.¹⁻³ Suitable spin traps are nitroso compounds (*e.g.* 2-methyl-2-nitrosopropane ⁴ and 2-methyl-2-nitrosobutan-3-one) and nitrones (*e.g.* phenyl-*N*-t-butyl nitrone).⁵ The general reactions to give nitroxide adducts from nitroso compounds and nitrones are

More recently, Janzen ⁶⁻⁸ has extended this method to the gas phase with the successful trapping of methyl, ethyl and perfluoroethyl radicals from the photolysis of acetone, tetraethyl lead and perfluoroazoethane respectively, and Kikkawa *et al.*⁹ have trapped short-lived free radicals formed from the glow discharge reaction of aromatic compounds. Other precursors have been investigated.⁷ The spin trap used by Janzen and co-workers was phenyl-*N*-t-butyl nitrone placed as a powder near the outlet from the photolysis vessel. Radicals trapped with 2-methyl-2-nitrosopropane were detected similarly, but this trap was prone to decomposition.

In the present work, 2-methyl-2-nitrosopropane vapour was found to trap organic radicals produced in a silent electric discharge, with acceptable levels of decomposition of the spin trap. The radicals and the spin trap were simultaneously condensed from the gas phase on to a cold surface at the temperature of liquid nitrogen.

EXPERIMENTAL

APPARATUS

A continuously pumped silent electric discharge between concentric glass tubes operating at pressures $<100 \text{ N m}^{-2}$ was used. Reactant gas was leaked continuously into the discharge, and the vapour of the spin trap was also leaked in continuously, carried in an excess

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of nitrogen. Fig. 1 shows the crucial part of the apparatus. Reactant gas entered through leak L_1 , passed through the silent electric discharge between glass tube Z and the outer glass tube, and was pumped away. The spin trap vapour entered through leak L_2 and was condensed, with radicals and reactant gas, on the cold finger F. The condensate was transferred, for e.s.r. examination, to the tube T.

Three Pyrex vacuum lines were used, with mercury diffusion pumps and liquid nitrogen traps. The first was for handling the reactant gas, the second for the vapour of the spin trap, and the third line pumped the ozoniser discharge. The dimensions of the ozoniser were: length 230 mm; inner tube 19.65 mm i.d., 24.0 mm o.d.; outer tube 26.7 mm i.d., 30.1 mm o.d. The electrodes making electrical contact with the glass were of aluminium foil. The outer electrode was outside the outer glass tube and was earthed; the inner electrode was inside the inner glass tube and was connected to a transformer giving 10 kV at 50 Hz. The cold finger was 20 mm from the end of the inner glass discharge tube.

MATERIALS

All liquids were of A.R. quality. Gases were from Air Products. Liquid hydrocarbons were passed through silica gel to remove water and all samples were distilled and degassed under vacuum before use. Emanuel Ltd. supplied 2-methyl-2-nitrosopropane.

EXPERIMENTAL METHOD

The leak L_1 (fig. 1) was calibrated for various pressures of the reactant gas or vapour in the reservoir. Typically, a pressure of 10^4 N m⁻² in the reservoir gave a pressure of 100 N m⁻² in the discharge tube.



FIG. 1.—Apparatus for radical trapping, showing inner glass discharge tube Z, cold finger F, inlets for the vapour of the spin trap (L_2) and the reactant gas (L_1) , and the e.s.r. tube T. S_1 and S_2 are sample holders for the spin trap.

To obtain a reasonable flow of 2-methyl-2-nitrosopropane from the spin trap handling line through leak L_2 a pressure of 10³ N m⁻² of nitrogen was maintained over the solid spin trap in sample holder S₁ which was heated to 45°C. To avoid photodecomposition of the nitroso-monomer, the entire apparatus was screened from laboratory light. The light from the discharge was usually negligible. About 3 mg of 2-methyl-2-nitrosopropane was distilled on to the cold finger during an experiment. To start an experiment, flow rates were adjusted and a discharge was set up with 7 to 9 kV applied and several mA of current passing. The duration of an experiment was $\frac{1}{2}$ to 3 h. At the end of an experiment the discharge was turned off and the apparatus brought to atmospheric pressure by filling with nitrogen. For a reactant which was a liquid at room temperature, the cold finger F was warmed to the melting point of the reactant and reactants with product dripped into the e.s.r. tube T positioned below

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the cold finger. Reactant formed the greatest part of the condensate on the cold finger. For a reactant gaseous at room temperature, a solvent (benzene or dichloromethane) was distilled on to the cold finger before the apparatus was brought to atmospheric pressure with nitrogen, and solvent plus products were collected in T. The e.s.r. spectrum of the contents of the tube T was recorded on a Varian E4 spectrometer.

RESULTS

The range of pressures which was used with liquid reactants was ~ 7 to 140 N m⁻². At low pressures a limit was imposed by the small quantity of radicals produced in the discharge and by the difficulty of maintaining the discharge. For

 TABLE 1.—RADICALS DETECTED FROM A SILENT ELECTRIC DISCHARGE BY TRAPPING WITH

 2-methyl-2-nitrosopropane

reactant compound	solvent	pressure in discharge/N m ⁻²	duration of expt./min	radicals trapped (hyperfine splittings in nitroxide spectra/mT)
CH_4	C_6H_6	2.7	180	none ^a
CH ₃ I	C_6H_6	6.7	180	none ^a
CH ₃ COCH ₃	CH ₃ COCH ₃	9.3	180	none ^a
C_2H_6	C_6H_6	13.3	135	none ^{<i>a</i>}
C_6H_6	C_6H_6	43	30	none ^a
$n-C_4H_{10}$	CH_2Cl_2	33	30	sec-butyl
				$(a_{\rm N} = 1.47 a_{\rm H} = 0.13)$
i-C4H10	C_6H_6	12	180	t-butyl
				$(a_{\rm N} = 1.52)$
$n-C_5H_{12}$	$n-C_{5}H_{12}$	31	30	$(C_2H_5)_2CH \cdot and/or$
				CH ₃ CHC ₃ H ₇ ^b
				$(a_{\rm N} = 1.48)$
				unknown radical
	_			$(a_{\rm N} = 2.75)$
hexane	hexane	40	30	sec-alkyl ^b
petroleum	petroleum			$(a_{\rm N} = 1.47)$
fraction	fraction	•	•	
cyclohexane	cyclohexane	28	30	cyclohexyl ^e
heptane	heptane	29	30	sec-alkyl
petroleum	petroleum			$(a_{\rm N} = 1.47)$
fraction	Iraction	0.0	240	
$C_6H_5CH_3$	$C_6H_5CH_3$	9.3	240	$C_6H_5CH_2$ "
avalamentadiana	avalamento diana	40	20	$(a_{\rm N} = 1.50 \ a_{\rm H} = 0.75)$
cyclopentadiene	cyclopentadiene	40	30	" COCI " (
CCI_4	CCI_4	0	180	$(\tau - 0.65)$
				$(a_{\rm N} = 0.03)$
				(a = 0.78)
i-C-H-CHO	J-C-H-CHO	67	90	$(u_{\rm N} = 0.78)$
1 031170110	1-031170110	0.7	20	$(a_{11} - 1.49) a_{12} - 0.14)$
				$(u_{\rm N} = 1.4) u_{\rm H} = 0.14)$
				$(a_{\rm N} = 0.78)$
i-C4H10	CeHe	13	180	t-butyl
	-00		200	$(a_N = 1.52)$
$+O_2$		13		"COR"
_				$(a_{\rm N}=0.75)$

^a Weak signals from di-t-butyl nitroxide were frequently observed. ^b Each line of the triplet was a broad and poorly resolved doublet ($a_H \simeq 0.1 \text{ mT}$). ^c See text. ^d Di-t-butyl nitroxide also present. ^e Complex mixture of dialkyl nitroxides observed. ^f R probably i-C₃H₇.

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high pressures of vapour of reactants which were liquid at room temperature, a limit was imposed by the volume of liquid condensed during an experiment and by the vapour pressure of the reactant used. For gaseous reactants the upper pressure limit was $\sim 10^3$ N m⁻² and arose when the spin trap vapour did not distil on to the cold finger, but was pumped away. Also, at high pressures second-order radical reactions became more important with the greater collision frequency.

Table 1 gives results for radicals produced and trapped from a variety of reactants. The smallest alkyl radicals trapped were sec-butyl from a discharge in n-butane and t-butyl from 2-methylpropane. Attempts to trap methyl and ethyl radicals were without success. No radical products were found from a discharge in benzene.



Fig. 2.—E.s.r. spectrum of the radical products of a silent electric discharge in 2-methylpropane trapped by 2-methyl-2-nitrosopropane.

When reactants with labile hydrogen atoms (aldehydes and cyclopentadiene) were used, reaction with the spin trap in solution occurred at room temperature when the condensate on the cold finger was warmed up. This was suppressed by cooling the solution from the cold finger, but it was not possible to determine the relative contributions from radicals trapped from the discharge and from the solution reaction.

Fig. 2 is the e.s.r. spectrum of the product of a discharge in 2-methylpropane and shows a triplet due principally to di-t-butyl nitroxide. This radical is also produced by the decomposition of 2-methyl-2-nitrosopropane and subsequent reaction with another molecule of this spin trap, and was observed as a contaminant in some of the



FIG. 3.—E.s.r. spectrum of the radical products of a silent electric discharge in a mixture of 2-methylpropane and oxygen trapped by 2-methyl-2-nitrosopropane.

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experiments (see table 1). Fig. 3 shows the effect of introducing oxygen into the discharge. A second triplet with $a_N = 7.5$ G was produced which is thought to be from an acyl alkylnitroxide [RCO(Bu^t)NO·] but the nature of R is not known. This radical seems to arise from the trapping of an oxygen-containing radical from the discharge and not from reaction between the spin trap and oxygen atoms, because a blank experiment with oxygen and nitrogen in the discharge yielded no nitroxide radical.



FIG. 4.—E.s.r. spectrum of the radical products of a silent electric discharge in cyclohexane trapped by 2-methyl-2-nitrosopropane.

Fig. 4 is the spectrum of the products of a discharge in cyclohexane trapped by 2-methyl-2-nitrosopropane and is consistent with the trapping of cyclohexyl radicals to give $C_6H_{11}(Bu^t)NO_{\cdot}$. An interesting result was obtained from the action of a discharge on CCl_4 vapour. Instead of the expected spectrum of the CCl_3 radical adduct $CCl_3(Bu^t)NO_{\cdot}$ ¹⁰ the spectrum shown in fig. 5 was produced.



FIG. 5.—E.s.r. spectrum of the radical products of a silent electric discharge in tetrachloromethane trapped by 2-methyl-2-nitrosopropane.

This consists of two nitrogen triplets with $a_N = 6.5$ G and $a_N = 7.8$ G. The first radical has a hyperfine splitting constant consistent with that of ClCO(Bu^t)NO. The production of this radical is discussed below. The second radical may be HOCO(Bu^t)NO. but a definite assignment could not be made.

DISCUSSION

THE LIFETIME THAT FREE RADICALS MUST HAVE IN ORDER TO BE TRAPPED

Short-lived radicals will not be trapped by the method described here. If all radicals recombine or react before they come into contact with the spin trap no spectrum of the adduct will be seen. However it is unclear whether combination of the

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radical and the spin trap occurs mainly in the gas phase or on the cold surface. There seems to be some evidence for reaction on the cold surface when tetrachloromethane is used in the discharge. At the end of an experiment the cold finger had a blue deposit which is the colour of unreacted 2-methyl-2-nitrosopropane monomer. This deposit, on warming to room temperature, rapidly turned brown and the solution gave an e.s.r. spectrum of a nitroxide. If the assumption is made that some combination of radical and spin trap occurs on the cold finger, then it is possible to calculate the minimum lifetime that a radical must have to be detected by considering viscous flow in the apparatus. This time is that needed for a radical to get from the discharge to the cold surface and is of the order of 10 ms. (The pressure difference from one end to the other of the discharge tube, causing flow of gas, was ~ 13 N m⁻²). This time is such that there may be some difficulty in trapping the more reactive radicals such as methyl. In fact, Janzen, Lopp and Morgan⁸ found difficulty in trapping methyl radicals from the gas phase with 2-methyl-2-nitrosopropane. Our failure to detect phenyl from benzene or acetyl from acetone may be due to too short lifetimes.

RADICAL ADDUCTS FROM TETRACHLOROMETHANE

The production of the chlorocarbonyl radical adduct $ClCO(Bu^{t})NO \cdot$ from a discharge in tetrachloromethane may arise from further reactions of an initial adduct $Cl_{3}C(Bu^{t})NO \cdot .^{10}$ Thus Camaggi, Holman and Perkins ¹¹ have proposed a sequence of reactions leading to the chlorocarbonyl radical adduct in which the carbonyl oxygen atom is delivered to a nitrone intermediate by a nitroxide radical. Another possibility is that CCl_{3} radicals in the gas phase decompose to CCl radicals, and a series of reactions of these radicals with Bu'NO gives the chlorocarbonyl nitroxide.

SELECTIVITY OF THE TRAPPING PROCESS

The reaction of 2-methyl-2-nitrosopropane in the experiments described above is quite selective, with only one or two radicals being observed in each experiment. In electric discharges, however, many products are formed. Gas chromatographic analysis of the gas issuing from a discharge in 2-methylpropane in our apparatus revealed 17 products, and 25 products have been detected from a discharge in n-hexane.¹² However with 2-methylpropane only one trapped radical, the 2-methylpropyl radical, is seen.

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