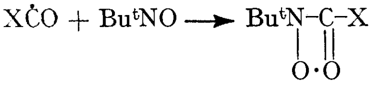
A Probe for Homolytic Reactions in Solution. Part VIII.[1] An Electron Spin Resonance Study of the Rates of Fragmentation and Spin Trapping of t-Butoxycarbonyl Radicals and Acyl Radicals

By **M. John Perkins,*** and **Brian P. Roberts,**† Department of Chemistry, Chelsea College, Manresa Road, London SW3 6LX

From a study of the competition between spin trapping and decarboxylation, the rate constant for addition of the t-butoxycarbonyl radical to 2-methyl-2-nitrosopropane (nitrosobutane) has been determined to be $1{\cdot}1 \times 10^{6}$ l mol^{-1} s^{-1} at 40° in di-t-butyl peroxide solvent. The rate constant in benzene must be very similar. Competitive scavenging and decarbonylation of a series of acyl radicals ($R\dot{C}O$) shows that the ease of loss of carbon monoxide increases along the series R = Me < Pr^{i} < adamantyl < Bu^{t} < $PhCH_2$. An absolute rate constant ($3{\cdot}9 \times 10^{3}$ s^{-1} at 40°) for the decarbonylation of $Pr^{i}\dot{C}O$ is obtained by assuming that this radical adds to nitrosobutane at the same rate as t-butoxycarbonyl. This rate constant is considerably smaller than that obtained previously in the gas phase and a possible source of error in the gas-phase value is identified. The formation of t-butoxy t-butyl nitroxide by addition of t-butoxyl radicals to nitrosobutane is reversible at ambient temperatures. Fragmentation of this nitroxide to give t-butoxyl radicals occurs with a rate constant of *ca.* $0{\cdot}14$ s^{-1} at 40°, whilst fragmentation with loss of t-butyl radicals is shown to occur by N–C, and not O–C, fission with a rate constant of *ca.* 10^{-3} s^{-1} at 40°.

In recent years the technique of spin trapping, that is scavenging of a reactive free radical by a diamagnetic molecule to give a more stable radical readily detectable by e.s.r. spectroscopy, has been employed extensively in qualitative studies of the mechanisms of homolytic organic reactions.[2] In contrast there have been relatively few reports of quantitative applications of this powerful mechanistic probe.

We now report the results of a quantitative study of the reaction of t-butoxycarbonyl radicals and acyl radicals with 2-methyl-2-nitrosopropane (nitrosobutane) [equation (1; X = $Bu^{t}O$ or alkyl)].

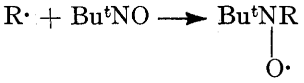


$$X\dot{C}O + Bu^{t}NO \longrightarrow \underset{O\cdot}{Bu^{t}N}-\underset{O}{\overset{\|}{C}}-X \qquad (1)$$

Under appropriate conditions a competition exists between reaction (1) and fragmentation of $X\dot{C}O$ [equations (2) and (3)]. The fragment alkyl radicals are also scavenged by nitrosobutane and from measurements of the concentrations of the nitroxides formed in reactions (1) and (4) the ratio of rates of spin trapping and fragmentation of the radical $X\dot{C}O$ may be obtained.

$$Bu^{t}O\dot{C}O \longrightarrow Bu^{t}\cdot + CO_2 \qquad (2)$$

$$R\dot{C}O \longrightarrow R\cdot + CO \qquad (3)$$



$$R\cdot + Bu^{t}NO \longrightarrow \underset{O\cdot}{\underset{|}{Bu^{t}NR}} \qquad (4)$$

RESULTS

A preliminary account of the kinetics of spin trapping of the t-butoxycarbonyl radical has already appeared.[3] When a solution containing nitrosobutane (*ca.* 0·1M), t-butyl formate (2M), and di-t-butyl hyponitrite (0·02M) (as a thermal source of t-butoxyl radicals) in benzene was warmed to 40° whilst the sample was in the cavity of the e.s.r. spectrometer, the spectrum shown in Figure 1 was obtained. Three different nitroxides are present in this spectrum, $Bu^{t}O{\cdot}N\dot{O}{\cdot}Bu^{t}$, *a*(N) 27·4 G (lines A); $Bu^{t}_{2}NO\cdot$, *a*(N) 15·5 G (lines B); $Bu^{t}O{\cdot}CO{\cdot}N\dot{O}{\cdot}Bu^{t}$ *a*(N) 8·7 G (lines C). The changes of radical concentration with time in a typical run are shown in Figure 2. Whilst the concentration of $Bu^{t}O{\cdot}N\dot{O}{\cdot}Bu^{t}$ (I) tended to reach a maximum value

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† *Present address:* Department of Chemistry, University College, 20 Gordon Street, London, WC1H 0AJ.

[1] Part VII, C. M. Camaggi and M. J. Perkins, *J.C.S. Perkin II*, 1972, 507.

[2] (*a*) M. J. Perkins in 'Essays on Free Radical Chemistry,' ed. R. O. C. Norman, *Chem. Soc. Special Publ. No.* 24, 1970, ch. 5; (*b*) E. G. Janzen, *Accounts Chem. Res.*, 1971, **4**, 31; (*c*) C. Lagercrantz, *J. Phys. Chem.*, 1971, 75, 3466.

[3] M. J. Perkins and B. P. Roberts, *J.C.S. Chem. Comm.*, 1973, 173.

within a short time, the concentrations of $\text{Bu}^t{}_2\text{NO}\cdot$ (II) and $\text{Bu}^t\text{O}\cdot\text{CO}\cdot\text{N}\dot{\text{O}}\cdot\text{Bu}^t$ (III) continued to increase linearly with time for the duration of the experiment.

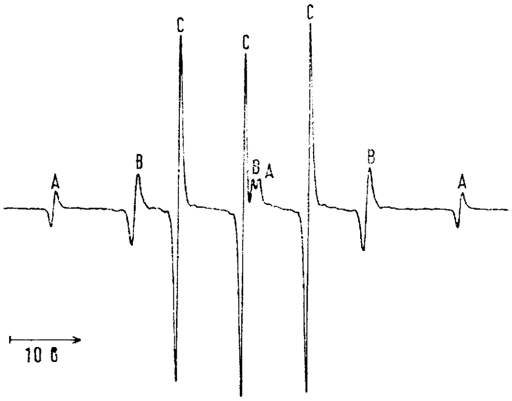

FIGURE 1 E.s.r. spectrum from the reaction of t-butoxyl radicals with t-butyl formate in the presence of nitrosobutane in benzene at 40°: A, $\text{Bu}^t\text{O}\cdot\text{N}\dot{\text{O}}\cdot\text{Bu}^t$; B, $\text{Bu}^t{}_2\text{NO}\cdot$; C, $\text{Bu}^t\text{O}\cdot\text{CO}\cdot\text{N}\dot{\text{O}}\cdot\text{Bu}^t$

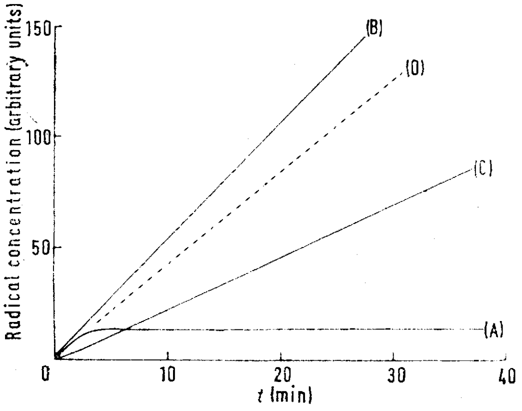

FIGURE 2 Plot showing the rates of build-up of nitroxides in the reaction of t-butoxyl radicals with t-butyl formate in the presence of nitrosobutane at 40°: (A), $\text{Bu}^t\text{O}\cdot\text{N}\dot{\text{O}}\cdot\text{Bu}^t$; (B), $\text{Bu}^t{}_2\text{NO}\cdot$; (C), $\text{Bu}^t\text{O}\cdot\text{CO}\cdot\text{N}\dot{\text{O}}\cdot\text{Bu}^t$; (D), $\text{Bu}^t{}_2\text{NO}\cdot$ corrected for decomposition of $\text{Bu}^t\text{O}\cdot\text{N}\dot{\text{O}}\cdot\text{Bu}^t$

When solutions containing t-butyl formate and nitrosobutane were heated to 40° no nitroxides were detected.* However, solutions containing di-t-butyl hyponitrite and nitrosobutane at 40° gave rise to both nitroxides (I) and (II). The fragmentation of (I) to give t-butyl radicals which are scavenged by nitrosobutane to give (II) has been reported previously.[4]

$$\text{Bu}^t\text{ON=NOBu}^t \xrightarrow{40^\circ} 2\text{Bu}^t\text{O}\cdot + \text{N}_2 \tag{5}$$

$$\text{Bu}^t\text{O}\cdot + \text{Bu}^t\text{OCHO} \longrightarrow \text{Bu}^t\text{OH} + \text{Bu}^t\text{O}\dot{\text{C}}\text{O} \tag{6}$$

$$\text{Bu}^t\text{O}\cdot + \text{Bu}^t\text{NO} \rightleftharpoons \underset{\text{(I)}}{\text{Bu}^t\text{O}\cdot\text{N}\dot{\text{O}}\cdot\text{Bu}^t} \tag{7}$$

$$\text{Bu}^t\text{O}\cdot\text{N}\dot{\text{O}}\cdot\text{Bu}^t \longrightarrow \text{Bu}^t\text{ONO} + \text{Bu}^t\cdot \tag{8}$$

$$\text{Bu}^t\cdot + \text{Bu}^t\text{NO} \longrightarrow \underset{\text{(II)}}{\text{Bu}^t{}_2\text{NO}\cdot} \tag{9}$$

$$\text{Bu}^t\text{O}\dot{\text{C}}\text{O} + \text{Bu}^t\text{NO} \longrightarrow \underset{\text{(III)}}{\text{Bu}^t\text{O}\cdot\text{CO}\cdot\text{N}\dot{\text{O}}\cdot\text{Bu}^t} \tag{10}$$

As expected on the basis of the above scheme, the average concentration of (I) was less in those experiments where a higher concentration of t-butyl formate was present. Although reaction (8) represents the most likely mode of fragmentation of (I) leading to t-butyl radicals,[4] it has been pointed out [5] that a β-scission is also possible [reaction (11)].

$$\text{Bu}^t\text{O}\cdot\text{N}\dot{\text{O}}\cdot\text{Bu}^t \longrightarrow \text{Bu}^t\text{NO}_2 + \text{Bu}^t\cdot \tag{11}$$

We set out to distinguish these two mechanisms by the use of $[^2\text{H}_9]$nitrosobutane. Thermolysis of di-t-butyl hyponitrite in the presence of $[^2\text{H}_9]$nitrosobutane gives $\text{t-C}_4\text{H}_9\text{-}\underset{\substack{|\\ \text{O}\cdot}}{\text{O}}\text{N-t-C}_4\text{D}_9$. Breakdown by reaction (8) followed by (9) will give $(\text{t-C}_4\text{D}_9)_2\text{NO}\cdot$, whereas (11) and (9) will produce $\text{t-C}_4\text{D}_9\cdot\text{N}\dot{\text{O}}\cdot\text{t-C}_4\text{H}_9$. In protic di-t-butyl nitroxide the e.s.r. line width is controlled by unresolved hyperfine interaction between the unpaired electron and the eighteen equivalent hydrogen atoms. Deuterium substitution thus decreases the line width in this nitroxide. Table 1 lists the line widths of the three possible isotopic forms of di-t-butyl nitroxide.

Fragmentation of $\text{t-C}_4\text{H}_9\text{O}\cdot\text{N}\dot{\text{O}}\cdot\text{t-C}_4\text{D}_9$ gave di-t-butyl nitroxide showing a peak-to-peak line width of 0·38 G. Reaction (8) is thus the major and probably the only, decomposition pathway giving t-butyl radicals at 40°. The small increase in line width over the value listed in Table 1 could be due to spin exchange broadening resulting from the presence of a relatively large concentration of t-butoxy t-butyl nitroxide.

TABLE 1

Line widths of the isotopically labelled forms of di-t-butyl nitroxide in benzene at +20°

Nitroxide	Source	Peak-to-peak line width (G)
$\text{t-C}_4\text{H}_9\underset{\substack{|\\ \text{O}\cdot}}{\text{N}}\text{t-C}_4\text{H}_9$	Photolysis of Bu^tNO	0·65 [a]
$\text{t-C}_4\text{H}_9\underset{\substack{|\\ \text{O}\cdot}}{\text{N}}\text{t-C}_4\text{D}_9$	Thermolysis of di-t-butyl hyponitrite in a 2M solution of t-butyl formate in benzene containing $\text{t-C}_4\text{D}_9\text{NO}$	0·53
$\text{t-C}_4\text{D}_9\underset{\substack{|\\ \text{O}\cdot}}{\text{N}}\text{t-C}_4\text{D}_9$	Photolysis of $\text{t-C}_4\text{D}_9\text{NO}$	0·35 [a]

[a] Addition of 2M-t-butyl formate had no effect on the line shapes.

By analogy with observations on alkoxy aryl nitroxides,[6] it has been suggested [2a] that the formation of t-butoxy t-butyl nitroxide may be reversible at ambient temperatures. When a solution of nitrosobutane in pure di-t-butyl peroxide was irradiated with u.v. light of wavelength *ca.*

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* With di-t-butyl peroxide as solvent very small concentrations of nitroxides could be detected in the absence of di-t-butyl hyponitrite. These probably arise by homolysis of the peroxide which could be detectable even at 40°. However, addition of a trace of t-butyl hydroperoxide increased the concentrations of nitroxides in the blank reactions and it is possible that this compound may be present to a minute extent even in purified di-t-butyl peroxide.

[4] A. Mackor, Th. A. J. M. Wajer, Th. J. de Boer, and J. D. W. van Voorst, *Tetrahedron Letters*, 1967, 385; A. Mackor, Th. A. J. W. Wajer, and Th. J. de Boer, *ibid.*, 1968, 1623.

[5] D. F. Bowman, J. L. Brockenshire, T. Gillan, and K. U. Ingold, *J. Amer. Chem. Soc.*, 1971, **93**, 6551.

[6] D. J. Cowley and L. H. Sutcliffe, *J. Chem. Soc.* (*B*), 1970, 569.

360 nm* at 40°, the concentration of t-butoxy t-butyl nitroxide increased to a limiting value, which was smaller in experiments where the concentration of nitrosobutane was lower. The limiting concentration of (I), at a given concentration of nitrosobutane, increased as the temperature decreased. When the light was shuttered the signal from (I) decayed with close to first-order kinetics at low nitrosobutane concentration, but in an irregular fashion at higher concentrations. Decay was more rapid at higher temperatures, and there was insufficient increase in the concentration of di-t-butyl nitroxide (II) during decay of (I) to account for removal of the latter solely by reaction (8). When adamantane (chosen because 1-adamantyl t-butyl nitroxide is very stable and its spectrum can be differentiated from that of di-t-butyl nitroxide) was added to the system the signal of (I) decayed much more rapidly than in its absence, and during decay of (I) when the light was shuttered the signal due to 1-adamantyl t-butyl nitroxide *increased*, although the increase was too large to be accounted for solely by the reverse of reaction (7) followed by hydrogen abstraction from adamantane by the t-butoxyl radicals. Similar increases in the concentration of the appropriate nitroxides were noted when ethylbenzene or t-butyl formate were present as hydrogen donors. The rate of decay of (I) at 40° was dependent upon the concentration of nitrosobutane at constant adamantane concentration (0·2M). With $[\mathrm{Bu^tNO}] = 0{\cdot}02\mathrm{M}$ the decay of (I) from *ca.* $10^{-5}\mathrm{M}$ followed first-order kinetics ($k_{\mathrm{obs}} = 8{\cdot}7 \times 10^{-2}\ \mathrm{s^{-1}}$) and was 95% complete in *ca.* 40 s, whereas with $[\mathrm{Bu^tNO}] = 0{\cdot}29\mathrm{M}$, decay of (I) from the same concentration was kinetically irregular and took >5 min.

We attribute these results to the reversibility of reaction (7), the rate constant k_{-7} being much larger than k_8. The rate of decay of (I) when the light is shuttered is thus dependent on the reaction removing t-butoxyl radicals from the system and, under our conditions, hydrogen abstraction is the most likely process responsible. If the concentration

$$\mathrm{Bu^tO\cdot} + \mathrm{RH} \longrightarrow \mathrm{Bu^tOH} + \mathrm{R\cdot} \qquad (12)$$

of (I) in the absence of irradiation is negligible and $k_{-7} \gg k_8$, the decay of (I) when the light is shuttered is given by equation (13).

$$\frac{-\mathrm{d}[(\mathrm{I})]}{\mathrm{d}t} = k_{-7}[(\mathrm{I})]\left\{1 - \frac{k_7[\mathrm{Bu^tNO}]}{k_{12}[\mathrm{RH}] + k_7[\mathrm{Bu^tNO}]}\right\} \qquad (13)$$

At low (<0·035M) concentrations of nitrosobutane in di-t-butyl peroxide containing hydroperoxide-free cumene (1M) the decay of (I) followed first-order kinetics. At 40° with $[\mathrm{Bu^tNO}] <$ *ca.* 0·01M the rate of decay of (I) did not increase any further as the nitrosobutane concentration decreased, and hence $k_{12}[\mathrm{RH}] \gg k_7[\mathrm{Bu^tNO}]$ under these conditions and $-\mathrm{d}[(\mathrm{I})]/\mathrm{d}t = k_{-7}[(\mathrm{I})]$. In this way k_{-7} was found to be *ca.* $0{\cdot}14\ \mathrm{s^{-1}}$ at 40° in di-t-butyl peroxide containing 1M-cumene. When $[\mathrm{Bu^tNO}]$ was 0·031M the observed first-order rate constant for decay of (I) was $4 \times 10^{-2}\ \mathrm{s^{-1}}$. Substitution of these values into equation (13) gives (k_7/k_{12}) as 80 at 40°. Unfortunately the rate constant for abstraction of hydrogen from any hydrocarbon by t-butoxyl radicals is not known with accuracy.[7] Taking k_{12} as *ca.* $10^5\ \mathrm{l\ mol^{-1}\ s^{-1}}$ gives k_7 *ca.* $8 \times 10^6\ \mathrm{l\ mol^{-1}\ s^{-1}}$ indicating that although the addition of t-butoxyl radicals to nitrosobutane is reversible it is still an extremely rapid reaction.

Before the competition between reactions (2) and (10) could be studied it was necessary to know the rate of fragmentation of t-butoxy t-butyl nitroxide to give t-butyl radicals. This was determined by experiments in the absence of t-butyl formate when, providing all the t-butyl radicals from reaction (8) are trapped to give di-t-butyl nitroxide which is stable under the reaction conditions, equation (14) holds (where 0 and t refer to time 0 and t, respectively). Only relative radical concentrations are

$$[(\mathrm{II})]_t - [(\mathrm{III})]_0 = k_8 \int_0^t [(\mathrm{I})]\mathrm{d}t \qquad (14)$$

required for the determination of k_8. The quantity $\int_0^t [(\mathrm{I})]\mathrm{d}t$ was evaluated graphically and the results are summarised in Table 2. Since $[(\mathrm{I})]$ changes relatively little during a given experiment, the best demonstration that its decomposition follows first-order kinetics is provided by experiments in which the average concentration of (I) is varied by use of different concentrations of di-t-butyl hyponitrite.

TABLE 2

Decomposition of t-butoxy t-butyl nitroxide

Temp. (°C)	Solvent	$[\mathrm{Bu^tNO}]/\mathrm{M}$ [a]	$[\mathrm{Bu^tON_2OBu^t}]/\mathrm{M}$	$k_8/\mathrm{s^{-1}}$
40	Benzene	0·074	0·016	$8{\cdot}2 \times 10^{-4}$
40	Benzene	0·152	0·016	$1{\cdot}0 \times 10^{-3}$
40	Benzene	0·055 [b]	0·013	$9{\cdot}1 \times 10^{-4}$
30	Benzene	0·083	0·016	$2{\cdot}5 \times 10^{-4}$
20	Benzene	0·091	0·016	$3{\cdot}8 \times 10^{-5}$
40	$\mathrm{Bu^tOOBu^t}$	0·084	0·0072	$1{\cdot}1 \times 10^{-3}$
40	$\mathrm{Bu^tOOBu^t}$	0·053	0·0014	$1{\cdot}2 \times 10^{-3}$
40	$\mathrm{Bu^tOOBu^t}$ [c]	0·067	0·0072	$1{\cdot}5 \times 10^{-3}$
40	$\mathrm{Bu^tOOBu^t}$ [d]	0·052	0·0072	$8{\cdot}0 \times 10^{-4}$

[a] Monomer concentration corrected for incomplete dissociation of dimer using K as in carbon tetrachloride (6·84 at 40° see ref. 31). [b] $[^2\mathrm{H}_9]$Nitrosobutane. [c] $\mathrm{Bu^tOH}$ (2·0M) also present. [d] EtOCHO (2·0M) also present in mixture; concentration of t-butoxy t-butyl nitroxide was low due to competitive reaction of t-butoxyl radicals with the formate (see text).

The results obtained in benzene at different temperatures may be expressed in terms of the Arrhenius equation (15), where $\theta = 2{\cdot}303RT$ kcal mol⁻¹. The independence of k_8 of nitrosobutane concentration supports the assumption that all the t-butyl radicals are scavenged by nitrosoalkane under our conditions.

$$\log (k_8/\mathrm{s^{-1}}) = 16{\cdot}0 - 27{\cdot}3/\theta \qquad (15)$$

The results in Table 2 suggest that k_8 will be essentially unaffected by the presence of t-butyl formate in di-t-butyl peroxide solvent, the latter being chosen for our present kinetic studies since it had been used as solvent in the earlier work on the rate of decarboxylation of the t-butoxycarbonyl radical.[8] In the presence of t-butyl formate it was therefore possible to correct the rate of formation of di-t-butyl nitroxide for that originating from the decomposition of (I) as shown in curve (D) of Figure 2.

If it is assumed that the only two reactions open to the

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* At this wavelength most of the light is absorbed by the peroxide although photolytic cleavage of nitrosobutane is not entirely eliminated.

[7] A. A. Zavitsas and J. D. Blank, *J. Amer. Chem. Soc.*, 1972, **94**, 4603; A. A. Zavitsas and J. A. Pinto, *ibid.*, p. 7390; J. A. Howard, *Adv. Rree Radical Chem.*, 1972, **4**, 49.

[8] D. Griller and B. P. Roberts, *J.C.S. Perkin II*, 1972, 747.

t-butoxycarbonyl radical are decarboxylation and addition to nitrosobutane [reaction (10)], and that (II) and (III) are not removed from the system, then equation (16) may be derived. Values of (k_{10}/k_2) may thus be evaluated and these are listed in Table 3.

$$\frac{[(\mathrm{III})]_t - [(\mathrm{III})]_0}{[(\mathrm{II})]_t - [(\mathrm{II})]_0 - k_8 \int_0^t [(\mathrm{I})]\mathrm{d}t} = \frac{k_{10}[\mathrm{Bu}^t\mathrm{NO}]}{k_2} \qquad (16)$$

TABLE 3

Competition between addition to nitrosobutane and decarboxylation of the t-butoxycarbonyl radical at 40°

$[\mathrm{Bu^tNO}]$/ M	$[\mathrm{Bu^tOCHO}]$/ M	$[\mathrm{Bu^tON_2OBu^t}]$/ M	Solvent	(k_{10}/k_2)/ l mol^{-1}
0·052	2·0	0·016	Benzene	12·2
0·079	2·0	0·016	Benzene	15·6
0·150	2·0	0·015	Benzene	10·0
0·103	3·1	0·016	Benzene	13·5
0·081	1·2	0·016	Benzene	48·0 [a]
0·035	2·0	0·011	$\mathrm{Bu^tOOBu^t}$	15·4
0·0034	2·0	0·0072	$\mathrm{Bu^tOOBu^t}$	12·6
0·078	2·0	0·0072	$\mathrm{Bu^tOOBu^t}$	8·1
0·046	2·0	0·0072	$\mathrm{Bu^tOOBu^t}$	9·6
0·154	2·0	0·0072	$\mathrm{Bu^tOOBu^t}$	10·0

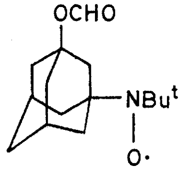
[a] At 30°.

At 40° in a 2M solution of t-butyl formate in di-t-butyl peroxide, the mean value of (k_{10}/k_2) was 11 ± 3 l mol^{-1}. Taking [8] $k_2 = 1{\cdot}0 \times 10^5$ s^{-1} at 40° we obtain $k_{10} = 1{\cdot}1 \times 10^6$ l mol^{-1} s^{-1} at 40°. It is not expected that a change of solvent from di-t-butyl peroxide to benzene would substantially alter k_{10}.

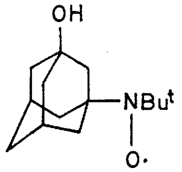
The assumptions made in deriving equation (16) are justified by the following observations. The rate of build-up of (II) and (III) were constant during the period of the experiments (see Figure 2) apart from small deviations around $t = 0$ which may be ascribed to temperature equilibration. The rate constant ratio (k_{10}/k_2) is essentially independent of the concentration of nitrosobutane present.

In experiments in which the nitroxide (II) and ethoxycarbonyl t-butyl nitroxide [9] (*ca.* 10^{-5}M) were added to a 2M solution of t-butyl formate in di-t-butyl peroxide or benzene at 40°, the intensities of their e.s.r. spectra did not decrease [in the case of (II)] or decayed sufficiently slowly for the process to be neglected [in the case of ethoxycarbonyl t-butyl nitroxide].

Similar experiments with 1-adamantyl formate were undertaken in the hope of examining the competition between spin trapping and decarboxylation of the 1-adamantyloxycarbonyl radical. At 40° the rate of build-up of 1-adamantyloxycarbonyl t-butyl nitroxide [*a*(N) 8·3 G] was very small, but the dialkyl nitroxide present was assigned the structure (IV) [*a*(N) 15·3 G; *a*(H) *ca.* 0·5 G (8H)] and was not the expected 1-adamantyl t-butyl nitroxide [10] [*a*(N) 15·3 G; *a*(H) *ca.* 0·5 G (9H)]. This result means that the two tertiary C–H bonds of the adamantane cage in the formate are more reactive towards hydrogen abstraction by t-butoxyl radicals than the CHO group. In order to confirm the structure of (IV) the nitroxide (V) [*a*(N) 15·4 G; *a*(H) *ca.* 0·5 G (8H)] was produced by spin trapping of the 3-hydroxy-1-adamantyl radical generated by abstraction of hydrogen from adamantan-1-ol. It should be pointed out that the e.s.r. signal from any small amount of 1-adamantyl t-butyl nitroxide resulting from decarboxylation of 1-adamantyloxycarbonyl radicals would be masked by the intense signal from (IV).



(IV)



(V)

Acyl Radicals.—Using a similar experimental procedure to that adopted above we have studied the competition between decarbonylation and addition to nitrosobutane of a series of acyl radicals derived by hydrogen abstraction from aldehydes.

$$\mathrm{Bu^tO\cdot} + \mathrm{RCHO} \longrightarrow \mathrm{R\dot{C}O} + \mathrm{Bu^tOH} \qquad (17)$$

$$\mathrm{R\dot{C}O} + \mathrm{Bu^tNO} \longrightarrow \underset{(\mathrm{VI})}{\mathrm{RCO{\cdot}N\dot{O}{\cdot}Bu^t}} \qquad (18)$$

$$\mathrm{R\dot{C}O} \longrightarrow \mathrm{R\cdot} + \mathrm{CO} \qquad (19)$$

$$\mathrm{R\cdot} + \mathrm{Bu^tNO} \longrightarrow \underset{(\mathrm{VII})}{\mathrm{R{\cdot}NO{\cdot}Bu^t}} \qquad (20)$$

With the aldehyde concentrations employed, formation of t-butoxy t-butyl nitroxide was not detected since reaction (17) is now much faster than reaction (6). From the rates of build-up of the nitroxides (VI) and (VII) it was possible to evaluate the ratio (k_{18}/k_{19}). Pivalaldehyde ($\mathrm{R} = \mathrm{Bu^t}$) was studied in most detail.

Nitroxide (VI; $\mathrm{R} = \mathrm{Bu^t}$) * [*a*(N) 8·1 G] decays slowly in the presence of pivalaldehyde at 40°, but the decay was sufficiently slow for it to be neglected at the aldehyde concentrations and rates of radical production used in our experiments. Di-t-butyl nitroxide (VII; $\mathrm{R} = \mathrm{Bu^t}$) decayed extremely slowly at 40° in the presence of pivalaldehyde. It should be noted that in these experiments the nitroxides were present in very low concentrations (*ca.* 10^{-6}—10^{-5}M) and it is not certain whether they were destroyed by reaction with the aldehyde (*e.g.* by hydrogen abstraction [11]) or by reaction with unknown impurities in the system. For the purposes of this study it was not necessary to know the mechanism of removal, but only to know that the rate of removal was slow under our reaction conditions.

Assuming that the only fate open to the t-butylcarbonyl radicals is addition to nitrosobutane or decarbonylation, and that all the t-butyl radicals produced are trapped, equation (21) may be derived ($\mathrm{R} = \mathrm{Bu^t}$).

$$\frac{[(\mathrm{VI})]_t - [(\mathrm{VI})]_0}{[(\mathrm{VII})]_t - [(\mathrm{VII})]_0} = \frac{k_{18}}{k_{19}}[\mathrm{Bu^tNO}] \qquad (21)$$

Plots of [(VI)] and [(VII)] against time were linear over a considerable range of concentrations after initial temperature equilibration. The results are set out in Table 4.

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* Prepared by nickel peroxide oxidation of the hydroxamic acid [8] from reaction of pivaloyl chloride with t-butyl hydroxylamine.

[9] M. J. Perkins and P. Ward, *J.C.S. Chem. Comm.*, 1973, 883.

[10] C. Morat and A. Rassat, *Bull. Soc. chim. France*, 1971, 891.

[11] For a similar reaction of bis(trifluoromethyl) nitroxide see R. E. Banks, D. R. Choudhury, and R. M. Haszeldine, *J.C.S. Perkin I*, 1973, 80.

TABLE 4

Competition between addition to nitrosobutane and decarbonylation of the t-butylcarbonyl radical at 40°

$[\mathrm{Bu^tNO}]$/ M	$[\mathrm{Bu^tCHO}]$/ M	$[\mathrm{Bu^tON_2OBu^t}]$/ M	Solvent	(k_{18}/k_{19})/ l mol^{-1}
0·018	0·623	0·005	Benzene	25·0
0·040	0·623	0·005	Benzene	20·8
0·087	0·623	0·005	Benzene	16·5
0·112	0·623	0·005	Benzene	18·6
0·250	0·623	0·005	Benzene	14·7
0·045	0·156	0·005	Benzene	25·8
0·051	0·312	0·005	Benzene	22·4
0·029	1·84	0·0014	Benzene	20·0
0·060	0·623	0·010	Benzene	27·4
0·076	0·623	0·005	$\mathrm{Bu^tOOBu^t}$	20·3

The mean value of (k_{18}/k_{19}) is 21 l mol^{-1} at 40° and appears unaffected by a change of solvent from benzene to di-t-butyl peroxide. The ratio (k_{18}/k_{19}) is also essentially independent of the concentration of aldehyde indicating that reaction (22) is unimportant. From gas-phase data on the

$$\mathrm{Bu^t\cdot + Bu^tCHO \longrightarrow Bu^t\dot{C}O + Bu^tH} \qquad (22)$$

abstraction of hydrogen from acetaldehyde by methyl radicals,[12] it may be estimated that k_{22} is $<$ *ca.* 2×10^3 l mol^{-1} s^{-1} at 40°, whereas k_{20} must be *ca.* 10^6 l mol^{-1} s^{-1} (see below). The possibility of alkyl and acyl radicals reacting with nitroxides present rather than with the nitrosobutane deserves some comment. This will only be important if it results in the *selective* removal of (VI), (VII), R·, or R$\dot{\mathrm{C}}$O and would manifest itself in the form of curvature of the plots of [(VI)] and [(VII)] against time, which was not detected at the nitroxide concentrations (10^{-6}—10^{-5}M) obtained in our experiments.

The results obtained with other aldehydes are listed in Table 5 together with the result for pivalaldehyde. In some cases only one nitroxide, (VI) or (VII), was detected and k_{18} was then too small or too large respectively to measure by this technique.

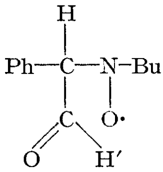
TABLE 5

Competition between addition to nitrosobutane and decarbonylation of acyl radicals in benzene at 40°

R in R$\dot{\mathrm{C}}$O	(k_{18}/k_{19})/ l mol^{-1}	k_{19}/s^{-1} [a]	$(k_{19})_{\mathrm{R\dot{C}O}}$ relative to $(k_{19})_{\mathrm{Pr^i\dot{C}O}}$ [b]
Me	Large [c]	Small [c]	$\ll 1$
$\mathrm{Pr^n}$	Large [c]	Small [c]	$\ll 1$
$\mathrm{Pr^i}$	280	$3{\cdot}9 \times 10^3$	(1)
$\mathrm{Bu^t}$	21	$5{\cdot}2 \times 10^4$	13·3
1-Adamantyl	57	$1{\cdot}9 \times 10^4$	4·9
$\mathrm{PhCH_2}$	$<0{\cdot}15$ [d]	$>7 \times 10^6$ [d]	>1870

[a] Taking $k_{18} = 1{\cdot}1 \times 10^6$ s^{-1} at 40° independent of R (see Discussion section). [b] Assuming $(k_{18})_{\mathrm{R\dot{C}O}} = (k_{18})_{\mathrm{Pr^i\dot{C}O}}$ at 40° (See Discussion section). [c] Only the acyl t-butyl nitroxide could be detected even with a very low concentration of nitrosobutane. [d] No acyl t-butyl nitroxide could be detected but maximum concentration could be estimated under high spectrometer gain.

With phenylacetaldehyde, in addition to benzyl t-butyl nitroxide an e.s.r. signal assigned to the nitroxide (VIII) [*a*(N) 14·6 G; *a*(H) 3·27 G (1H); *a*(H′) 1·32 G (1H)] was a major feature of the spectrum. It is possible that (VII) was formed by addition of the benzylic C–H bond of the aldehyde to the nitrosoalkane followed by oxidation of the resulting hydroxylamine, since its relative concentration


(VIII)

increased with the concentration of nitrosobutane present. Even with very high nitrosobutane concentrations no benzylcarbonyl t-butyl nitroxide could be detected.

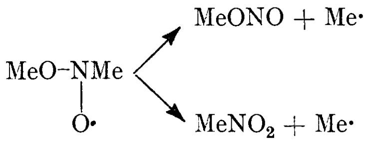
Adamantane-1-carbaldehyde gave (VI; R = 1-adamantyl) [*a*(N) 8·1 G] and (VII; R = 1-adamantyl) [*a*(N) 15·3 G; *a*(H) *ca.* 0·5 G (9H)]. When [^{2}H$_9$]nitrosobutane was employed, no 3-formyl-1-adamantyl t-butyl nitroxide could be detected (*cf.* previous results with adamantyl formate).

DISCUSSION

The formation of t-butoxy t-butyl nitroxide by addition of t-butoxyl radicals to nitrosobutane is readily reversible at ambient temperatures although it is still a very rapid process with a rate constant similar to that for addition of carbon-centred radicals to the nitrosoalkane. An alkoxy alkyl nitroxide is probably an intermediate in the overall homolytic displacement of an alkoxyl radical from an alkyl nitrite by an alkyl radical.[13]

$$\mathrm{R^1\cdot + R^2ONO \longrightarrow R^2O{\cdot}N\dot{O}{\cdot}R^1 \longrightarrow R^2O\cdot + R^1NO} \qquad (23)$$

Fragmentation of t-butoxy t-butyl nitroxide to give t-butyl radicals occurs by N–C and not C–O fission. For the related radical methoxy methyl nitroxide it may be calculated [14] that the two pathways for decomposition are thermodynamically very similar. At 40° reaction (24b) involves the more favourable free energy change, but by only *ca.* 1 kcal mol^{-1}.



(24a)

(24b)

The addition of a t-butoxycarbonyl radical to nitrosobutane is a very rapid reaction, amongst some of the fastest radical–molecule reactions for which rate data are available. Addition of carbon-centred radicals to alkenes in the gas phase usually [15] involves *A* factors of about 10^8 l mol^{-1} s^{-1}. Assuming addition to nitrosobutane has a similar *A* factor we estimate an activation energy of between 2 and 3 kcal mol^{-1}, which compares with *ca.* 6 kcal mol^{-1} for the addition of alkyl radicals to alkenes,[15] and with 2·4 kcal mol^{-1} for the addition of trifluoromethyl radicals to ethylene.[13]

Janzen *et al.*[16] have estimated the rate constant for the

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[12] K. J. Laidler and M. T. H. Liu, *Canad. J. Chem.*, 1968, **46**, 479.

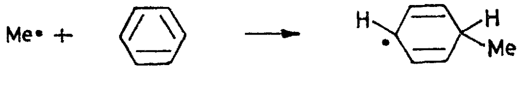
[13] K. U. Ingold and B. P. Roberts, ' Free Radical Substitution Reactions,' Wiley-Interscience, New York, 1971.

[14] From data given by S. W. Benson ' Thermochemical Kinetics,' Wiley, New York, 1968.

[15] J. A. Kerr in ' Free Radicals ' ed. J. K. Kochi, Wiley-Interscience, New York, 1973, vol. 1, ch. 1.

[16] E. G. Janzen, C. A. Evans, and Y. Nishi, *J. Amer. Chem. Soc.*, 1972, **94**, 8236.

addition of benzoyloxyl radicals to benzylidene-t-butylamine *N*-oxide to be 10^5—10^6 l mol^{-1} s^{-1} at 40°, indicating that nitrosobutane and the *N*-oxide have similar efficiences in the spin-trapping reaction, although a rate constant of 6×10^7 l mol^{-1} s^{-1} has been deduced recently for the addition of methoxyl radicals to this *N*-oxide in methanol at 25°.[17] We have investigated briefly the competition between decarboxylation of the t-butoxycarbonyl radical and its addition to benzylidene-t-butylamine *N*-oxide. Overlapping spectra are a great problem in this system but the rate constant for addition appears to be close to 10^6 l mol^{-1} s^{-1}. Heilman *et al.*[18] have determined the relative reactivities of benzene and nitrosobenzene towards methyl radicals at 65°. These authors found (k_{26}/k_{25}) was *ca.* 10^5, and taking[19] k_{25} *ca.* 50 l mol^{-1} s^{-1} we estimate that k_{26} is between 10^6 and 10^7 l mol^{-1} s^{-1} at 65°.



(25)

(26)

The results with 1-adamantyl formate highlight an important advantage of the spin-trapping method for the identification of reactive radical intermediates which are difficult to detect directly for one reason or another (*e.g.* rapid radical–substrate or –solvent reactions, spectral multiplicity giving rise to low intensity, broad resonance lines). The 3-formyloxy-1-adamantyl radical, which spin trapping demonstrates is the major product of reaction of t-butoxyl radicals with 1-adamantyl formate, was not detected when di-t-butyl peroxide was photolysed with high intensity u.v. light in the presence of the formate, whereas the 1-adamantyloxycarbonyl radical was detected.[8] The spectrum of the alkoxycarbonyl radical consists of one line whilst that of the 3-formyloxy-1-adamantyl radical must be very complex,[20] making it much more difficult to detect at a given concentration.

There are no *direct* measurements of the rates of decarbonylation of acyl radicals in gas or solution phases. Estimates of decarbonylation rates have been made in both phases relative to some other radical–radical or radical–molecule reaction. Applequist and Kaplan[21] measured the rate of decarbonylation relative to the rate at which the acyl radical abstracted chlorine from carbon tetrachloride. These authors found that $\mathrm{Bu^t\dot{C}O}$ lost carbon monoxide 10·8 times more readily than $\mathrm{Pr^i\dot{C}O}$ at 135°. If this ratio is extrapolated to 40° assuming the two decarbonylations have similar *A* factors we obtain a relative reactivity of 22, in good agreement with our value from spin trapping. Applequist and Kaplan had to assume that the rate of abstraction of chlorine from carbon tetrachloride was independent of the nature of the acyl radical. Similarly, in comparing rates of decarbonylation we must assume that the rate of addition of acyl radicals to nitrosobutane is independent of the nature of the acyl group. Since the addition process is very rapid with a low activation energy this is a reasonable assumption for such similar radicals.

The assumption that the rate of chlorine abstraction from carbon tetrachloride is independent of the nature of the acyl radical is perhaps less satisfactory. Applequist and Kaplan found that 1-adamantylcarbonyl radical lost carbon monoxide 2·5 times more readily than did $\mathrm{Bu^t\dot{C}O}$ at 135°, and this relative reactivity becomes 5·2 at 40°, in contrast with our value of 0·4 from spin trapping. The ease of loss of carbon monoxide from $\mathrm{R\dot{C}O}$ follows the order of stability of the alkyl radical formed (primary < secondary < tertiary < benzyl). Our results can be taken to indicate that the 1-adamantyl radical is somewhat less stable than t-butyl, in agreement with previous work on the rates of thermolysis of peroxyesters $\mathrm{R{\cdot}CO{\cdot}OOBu^t}$,[22,23] and azoalkanes RN=NR,[24] and the rates of fragmentation of the radicals $\mathrm{Ph\dot{C}(H)OR}$[25] (R = $\mathrm{Bu^t}$ or 1-adamantyl.)

Robbins and Eastman[26] measured the rate of decarbonylation of the benzylcarbonyl radical relative to its rate of scavenging by a stable dialkyl nitroxide. Assuming that the rate constant for scavenging was 10^9 l mol^{-1} s^{-1} these authors found that k_{27} was *ca.* 10^8 s^{-1} in benzene at room temperature. This result is consistent with our minimum value of k_{27} of 7×10^6 s^{-1} at 40°.

$$\mathrm{PhCH_2\dot{C}O} \longrightarrow \mathrm{PhCH_2{\cdot}} + \mathrm{CO} \qquad (27)$$

Extrapolation to 40° of the gas-phase data[27] for the rate constant for decarbonylation of the acetyl radical gives k_{28} *ca.* 1 s^{-1}. Clearly our inability to detect methyl t-butyl nitroxide in spin-trapping experiments on hydrogen abstraction from acetaldehyde is consistent with this rate constant.

$$\mathrm{Me\dot{C}O} \longrightarrow \mathrm{Me{\cdot}} + \mathrm{CO} \qquad (28)$$

The *absolute* rate constants for decarbonylation of acyl radicals listed in Table 5 were obtained with the assumption that these radicals add to nitrosobutane with the same rate constant as that for scavenging of t-butoxycarbonyl radicals. Such an assumption is very reason-

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[17] P. Ledwith, P. J. Russell, and L. H. Sutcliffe, *Proc. Roy. Soc.*, 1973, *A*, **332**, 151.

[18] W. J. Heilman, A. Rembaum, and M. Szwarc, *J. Chem. Soc.*, 1957, 1127.

[19] D. F. DeTar, *J. Amer. Chem. Soc.*, 1967, **89**, 4058.

[20] P. J. Krusic, T. A. Rettig, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1972, **94**, 995.

[21] D. E. Applequist and L. Kaplan, *J. Amer. Chem. Soc.*, 1965, **87**, 2194.

[22] J. P. Lorand, S. D. Chodroff, and R. W. Wallace, *J. Amer. Chem. Soc.*, 1968, **90**, 5266.

[23] R. C. Fort, jun., and R. E. Franklin, *J. Amer. Chem. Soc.*, 1968, **90**, 5267.

[24] M. Prochazka, O. Ryba, and D. Lim, *Coll. Czech. Chem. Comm.*, 1968, **33**, 3378.

[25] W. H. Chick and S. H. Ong, *Chem. Comm.*, 1969, 216.

[26] W. K. Robbins and R. H. Eastman, *J. Amer. Chem. Soc.*, 1970, **92**, 6077.

[27] S. W. Benson and H. E. O'Neal, Kinetic Data on Gas Phase Unimolecular Reactions, NSRDS-NBS 21, Washington, 1970.

able for such structurally similar radicals.* Direct comparison of these absolute rate constants with gas-phase data is possible in the case of the isopropylcarbonyl radical.[29] This radical was generated by abstraction of hydrogen from isobutyraldehyde by difluoroaminyl radicals between 80 and 150°, and the rate of decarbonylation of $\mathrm{Pr^i\dot{C}O}$ was determined relative to its rate of reaction with $\mathrm{\dot{N}F_2}$ radicals.[29] The result in the high pressure limit is summarised in equation (31).[29]

$$\mathrm{Pr^i\dot{C}O} \longrightarrow \mathrm{Pr^{i\cdot}} + \mathrm{CO} \qquad (29)$$

$$\mathrm{Pr^i\dot{C}O} + \mathrm{\dot{N}F_2} \longrightarrow \mathrm{Pr^iCO{\cdot}NF_2} \qquad (30)$$

$$\log\,[(k_{29}/k_{30})/\mathrm{mol\ l^{-1}}] = 2{\cdot}02 - 9{\cdot}75/\theta \qquad (31)$$

The authors assumed that $k_{30} = 10^{11}$ l mol^{-1} s^{-1} independent of temperature, which gives $k_{29} = 1{\cdot}5 \times 10^6$ s^{-1} at 40°. This is considerably larger than our value in solution ($3{\cdot}9 \times 10^3$ s^{-1}). Part of this difference may be due to the phase change, but we believe that the gas-phase value is too high. In view of the recent work of Benson and his co-workers [30] on the rates of self-reaction of alkyl radicals in the gas phase it is clear that the assumption of $k_{30} = 10^{11}$ l mol^{-1} s^{-1} is probably incorrect. Except for methyl radicals the A factors for radical self-reaction are *ca.* $10^{9.5}$ l mol^{-1} s^{-1} and some combinations appear to require significant activation energies. We believe that k_{30} is probably between 10^8 and 10^9 l mol^{-1} s^{-1} at 40° which would bring the gas-phase value of k_{29} into agreement with our result in solution. The A factor accepted [27] for decarbonylation of the acetyl radical in the gas phase is $10^{10.3}$ s^{-1}. With revision of the accepted values of the rate constants for radical–radical reactions in the gas phase the A factors for decarbonylation of the higher acyl radicals will move closer to the low value for acetyl.

EXPERIMENTAL

Reagents.—Nitrosobutane was prepared by oxidation of t-butylamine with hydrogen peroxide.[31] [^{2}H$_9$]Nitrosobutane was prepared by R. J. Holman. Commercial di-t-butyl peroxide was washed with acidic potassium iodide solution, then with water, and after drying ($\mathrm{MgSO_4}$) and distillation was passed down a column of basic alumina (Woelm activity I). Analytical reagent benzene was dried over sodium and distilled. t-Butyl formate was prepared by the method of Stevens and Van Es [32] and 1-adamantyl formate was prepared similarly.[8] Di-t-butyl hyponitrite was synthesised according to the method of Kiefer and Traylor.[33] Adamantane-1-carbaldehyde was prepared by reduction of the acid chloride with lithium tributoxyaluminium hydride.[21] Other aldehydes were commercial products which were trap-to-trap distilled under vacuum and stored under nitrogen at 5°.

E.s.r. Spectroscopy.—A Varian E-4 instrument was used with a standard variable temperature accessory. The sample temperature was measured with a copper–constantan thermocouple. The magnetic field sweep of the spectrometer was calibrated using a solution of Fremy's salt in saturated aqueous sodium carbonate [34] [a(N) 13·091 G]. All experiments with nitrosobutane monomer were performed in darkness or subdued light and under nitrogen. Three types of sample preparation were employed and all gave similar results.

(i) Standard fused silica 4 mm o.d. tubes were fitted with a wider (10 mm) neck to take a wired-on, self-sealing rubber cap. Nitrosobutane was weighed in as the solid dimer and kept cold whilst the tube was evacuated and refilled with nitrogen through a hypodermic needle passed through the rubber cap. Solvent and t-butyl formate or aldehyde (previously deoxygenated) were then added by syringe and the nitrosobutane left to dissociate (10 min). The t-butyl hyponitrite was then added in the form of a deoxygenated solution in benzene (*ca.* 0·2M) and the tube briefly and vigorously shaken to mix the contents and the sample inserted into the cavity of the spectrometer at room temperature. After setting up the spectrometer the temperature was increased to 40° and the nitroxide resonance lines repeatedly scanned recording the spectra on an auxiliary strip chart recorder to give a time axis. Concentrations of radicals were either taken as proportional to the first moment of the derivative curve or were determined by electronic integration of the derivative curve.[35] In experiments where the concentration of nitrosobutane was very small the dimer was dissolved in a larger volume of solvent and the required volume of solution syringed into the sample tube.

In some experiments it was noted that prolonged contact of the sample with the rubber cap led to a low initial rate of build-up of the alkoxycarbonyl t-butyl nitroxide but such cases were easily recognisable.

(ii) A technique similar to (i) was used except that between the rubber cap and the 4 mm o.d. silica tube a Rotaflo tap with a Teflon stopper was fitted so that the solution never came into contact with the rubber cap.

(iii) The reagents were mixed in a simple 4 mm o.d. silica sample tube and purged with nitrogen for 2 min using a fine capillary tube and the sample tube was then closed with a plug of Plasticine. Longer purging times did not improve resolution and tended to reduce the concentration of nitrosobutane in solution by removing the volatile monomer. For this reason this procedure was not employed in quantitative experiments where it was necessary to know the concentration of nitrosobutane exactly.

When di-t-butyl peroxide was used as solvent for the reaction of t-butoxyl radicals with nitrosobutane, in the absence of t-butyl formate or aldehydes, small concentrations of other nitroxides were present in addition to (I) and (II). The relative concentrations of (I) and (II) could still be accurately determined and the validity of the kinetic equations is not affected providing the unidentified nitroxides do not react with (II) or trap t-butyl radicals more efficiently than nitrosobutane (see Results section). When t-butyl formate or an aldehyde was present, the concentration of

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* The di-t-butoxymethyl radical adds to nitrosobutane with a rate constant of $8{\cdot}4 \times 10^5$ l mol^{-1} s^{-1} at 40°.[28]

[28] M. J. Perkins and B. P. Roberts, unpublished data.

[29] P. Cadman, C. Dodwell, A. F. Trotman-Dickenson, and A. J. White, *J. Chem. Soc.* (*A*), 1970, 2371.

[30] See H. E. O'Neal and S. W. Benson, in 'Free Radicals,' ed. J. K. Kochi, Wiley-Interscience, New York, 1973, vol. 2, ch. 17.

[31] J. C. Stowell, *J. Org. Chem.*, 1971, **36**, 3055.

[32] W. Stevens and A. Van Es, *Rec. Trav. chim.*, 1964, **83**, 1287.

[33] H. Kiefer and T. G. Traylor, *Tetrahedron Letters*, 1966, 6163.

[34] R. J. Faber and G. K. Fraenkel, *J. Chem. Phys.*, 1965, **43**, 4191.

[35] R. Barr, R. J. Holman, and M. J. Perkins, *Chem. and Ind.*, 1972, 43.

the unidentified nitroxides decreased to a negligible value, presumably because the t-butoxyl radicals were diverted from reaction with the peroxide solvent, or an impurity in it, to reaction with the formate or aldehyde.

Photolytic experiments employed the Varian 100 W mercury lamp accessory, the light from which was passed through a Chance OX1 filter and then through a solution of aqueous copper sulphate.

We are grateful to the S.R.C. for grants in support of this work.

[3/1780 *Received, 24th August, 1973*]