Spin Trapping: The Rate of Addition of t-Butoxycarbonyl Radicals to 2-Methyl-2-nitrosopropane ('t-Nitrosobutane')

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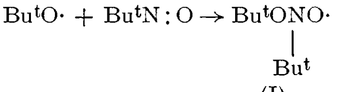
Summary The second-order rate constant for the title reaction has been determined to be $1{\cdot}1 \times 10^{6}$ l mol^{-1} s^{-1} in di-t-butyl peroxide at 40°.

Although spin trapping, *i.e.* the formation of relatively long-lived radicals by radical addition to diamagnetic scavengers (*e.g. C*-nitroso-compounds and nitrones) is now a widely recognised technique in free-radical chemistry,[1] little quantitative information is available regarding the reactivities of the various scavengers in the additional step.†

The only figure for the rate of radical addition to a *C*-nitroso-compound appears to be the approximate value for addition of methyl radicals to nitrosobenzene (10^{6}—10^{7} l mol^{-1} s^{-1} at 65°) which can be deduced from Szwarc's methyl affinity data[3] and an estimate of the rate of addition of methyl radicals to benzene.[4]

It seemed possible that rate data for related reactions might be obtained by studying the build-up of spin-adducts of radicals R· and R′· during competition between a unimolecular reaction of R· (→ R′·) of known rate, and the bimolecular scavenging of R· by the spin trap. Our initial studies of this possibility have been with the widely used scavenger t-nitrosobutane, and we have now obtained reproducible results in the case of R· = $\mathrm{Bu^tO\dot{C}O}$. These butoxycarbonyl radicals were generated by hydrogen abstraction from t-butyl formate using t-butoxyl radicals produced by thermolysis of di-t-butyl hyponitrite. Arrhenius parameters for unimolecular decarboxylation of $\mathrm{Bu^tO\dot{C}O}$[equation (5)] are known with some precision.[5] Furthermore the particular nitroxide spin-adducts formed by addition of both alkoxycarbonyl radicals[6] and the fragment radicals R′· (=$\mathrm{Bu^{t}\cdot}$) to nitrosobutane are especially long-lived, thus minimising possible complications from bimolecular decay of the spin adducts.

A difficulty with the above procedure is that butoxyl radicals are themselves trapped by nitrosobutane, and the resulting adduct (I) fragments to give butyl radicals.[7] The kinetics of this fragmentation were therefore examined in the absence of t-butyl formate in order that a correction could be made to the results obtained in its presence. For these experiments it was assumed that all the t-butyl radicals are scavenged by nitrosobutane and that the nitroxide (II) is not removed from the system. With these assumptions, the relationship $[(\mathrm{II})]_t - [(\mathrm{II})]_0 = k_2\int_0^t [(\mathrm{I})]\,\mathrm{d}t$ may be derived (where 0 and t refer to time 0 and time t, respectively). In all calculations the first moments (**M**) of the derivative spectra were taken as proportional to radical concentrations, employing the low-field lines of the nitroxides (I)—(III) which were well separated. A plot of $\{(\mathbf{M}_{(\mathrm{II})})_t - (\mathbf{M}_{(\mathrm{II})})_0\}$ against $\int_0^t \mathbf{M}_{(\mathrm{I})}\,\mathrm{d}t$ (evaluated graphically) was linear over a period sufficient for a tenfold increase in $\mathbf{M}_{(\mathrm{II})}$. From the slope of this, the value of k_2 at 40° in



$$\mathrm{Bu^tO\cdot + Bu^tN{:}O \rightarrow Bu^tO\underset{\substack{|\\ Bu^t}}{N}O\cdot} \tag{1}$$

(I)

$$\mathrm{(I) \rightarrow Bu^tONO + Bu^{t}\cdot} \tag{2}$$

$$\mathrm{Bu^{t}\cdot + Bu^tN{:}O \rightarrow \underset{(II)}{(Bu^t)_2NO\cdot}} \tag{3}$$

$$\mathrm{Bu^tO\cdot + Bu^tOCHO \rightarrow Bu^tOH + Bu^tO\dot{C}O} \tag{4}$$

$$\mathrm{Bu^tO\dot{C}O \rightarrow Bu^{t}\cdot + CO_2} \tag{5}$$

$$\mathrm{Bu^tO\dot{C}O + Bu^tN{:}O \rightarrow \underset{(III)}{Bu^tOCON(Bu^t)O\cdot}} \tag{6}$$

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† Since this communication was submitted, a paper by Janzen *et al.*[2] has appeared in which the rate constant for spin-trapping of benzoyloxy radicals by phenyl t-butyl nitrone has been estimated to be 10^{5}—10^{6} l mol^{-1} s^{-1} at 40°

di-t-butyl peroxide solvent was calculated as $1{\cdot}1 \pm 0{\cdot}3 \times 10^{-3}\,s^{-1}$, independent of nitrosobutane concentration (0·052—0·152M) and of the average concentration of (I) (varied by a factor of four by changing the concentration of di-t-butyl hyponitrite). From reactions between 20 and 40° in benzene, the temperature dependence of k_2 may be approximated by the equation $\log(k_2/s^{-1}) = 16{\cdot}0 - 27{\cdot}3/\theta$, where $\theta = 2{\cdot}303\,RT$ kcal mol^{-1}. The independence of k_2 of nitrosobutane concentration in both solvents supports the assumption that all the t-butyl radicals are scavenged by the nitrosoalkane under our conditions.

In the presence of t-butyl formate, and with the additional assumption that scavenging [equation (6)] and decarboxylation [equation (5)] are the only reactions open to butoxycarbonyl radicals, the relationship $k_6/k_5 = \{[(\mathrm{III})]_t - [(\mathrm{III})]_0\}/(\{[(\mathrm{II})]_t - [(\mathrm{II})]_0 - k_2\int_0^t[(\mathrm{I})]\mathrm{d}t\}[\mathrm{Bu^tN{:}O}])$ may be derived. For reaction times of *ca.* 30 min a plot of $\{(\mathbf{M}_{(\mathrm{II})})_t - (\mathbf{M}_{(\mathrm{III})})_0\}$ against $\{(\mathbf{M}_{(\mathrm{II})})_t - (\mathbf{M}_{(\mathrm{II})})_0 - k_2\int_0^t\text{-}\mathbf{M}_{(\mathrm{I})}\mathrm{d}t\}$ gave a straight line from the slope of which k_6/k_5 could be determined.

In order to minimise errors from solvent effect, k_6/k_5 was determined in di-t-butyl peroxide, which had previously been employed as solvent for the determination of k_5.[‡] At 40° the ratio k_6/k_5 was essentially independent of nitrosobutane concentration (0·0034—0·154M) and equal to 11 ± 3 l mol^{-1}. Extrapolation from the published data gives k_5 (40°) $= 1{\cdot}0 \times 10^5\,s^{-1}$, whence k_6 (40°) $= 1{\cdot}1 \times 10^6$ l mol^{-1} s^{-1} in a 2M solution of t-butyl formate in di-t-butyl peroxide. The rate constant for the addition reaction in benzene is probably very similar.

Preliminary experiments with the nitrone $\mathrm{PhCH{=}N(\rightarrow O)Bu^t}$ indicate that the rate constant for its reaction with butoxycarbonyl radicals is also *ca.* 10^6 l mol^{-1} s^{-1}.

In the course of the earlier work on decarboxylation of butoxycarbonyl radicals,[5] a parallel investigation of 1-adamantyloxycarbonyl radicals had been undertaken. However no 1-adamantyl radicals could be detected. Utilisation of the spin-trapping method with this system has revealed the unexpected result that butoxyl radicals abstract hydrogen from the 3-position of the adamantane nucleus far more readily than they do from the formyl group. Probably the 3-formyloxy-1-adamantyl radicals thus formed escaped detection in the earlier work because of the complexity (and consequent low signal strength) of their e.s.r. spectra.

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[‡] The correction term $k_2\int_0^t\mathbf{M}_{(\mathrm{I})}\mathrm{d}t$, which was usually small, was calculated using $k_2 = 1{\cdot}1 \times 10^{-3}\,s^{-1}$. The magnitude of k_2 is not expected to be greatly influenced by the presence of t-butyl formate. In di-t-butyl peroxide containing ethyl formate (2M) k_2 (40°) $= 8{\cdot}0 \times 10^{-4}\,s^{-1}$; with t-butyl alcohol (2M) k_2 (40°) $= 1{\cdot}5 \times 10^{-3}\,s^{-1}$.

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