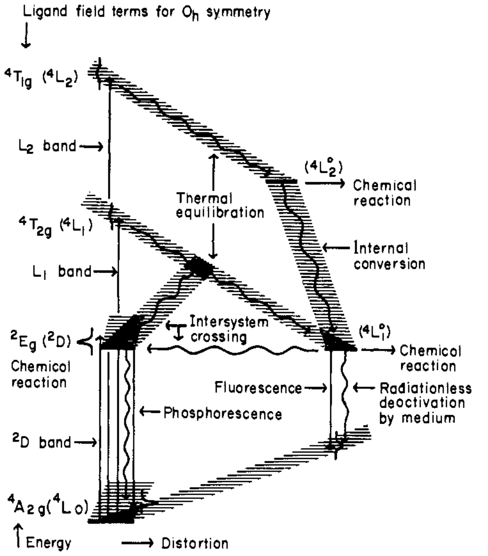

Figure 1. Energy level diagram (lowest levels) for a Cr(III) complex.

respectively. Released chloride ion was determined potentiometrically. Assuming that any Cr–N bond breaking would generate a weakly basic function, the upper limit to such bond breaking was inferred from the lack of detectable pH change on irradiation. The isomer composition of the product and the degree of isomerization of B were estimated from the spectral change on irradiation. The thermal aquation rate is negligibly slow at 22°.[15]

We find ϕ_{Cl^-} to be 6.9×10^{-4} and 7.7×10^{-4} on irradiation of the L_1 and L_2 bands, respectively, or about 400 times smaller than for A. The quantum yield for hydrogen ion uptake is $<10^{-3}$. More than 90% of the photoproduct is in the trans configuration (presumably *trans*-$Cr(cyclam)(OH_2)Cl^{2+}$); the quantum yield for *cis*-$Cr(cyclam)Cl_2^+$ is $<5 \times 10^{-4}$ at either wavelength. Preliminary results with 254-nm light are that only chloride aquation occurs, but now with a yield of about 0.2.

The photochemistry of non-O_h Cr(III) complexes appears to occur through reaction of the thermally equilibrated first excited quartet state, $^4L_1^0$,[16,17] rather than of the state immediately produced by light absorption, $^4L_1$, or the first doublet state, ^2D. A scheme of excited-state processes is shown in Figure 1.[16]

The photoinertness of B could have a photophysical explanation. Thus the radiationless deactivation $^4L_1^0 \rightarrow {}^4L_0$ might be unusually rapid; alternatively, the intersystem crossing $^4L_1 \rightarrow {}^2D \rightarrow {}^2D^0$ might be unusually efficient, with the latter state again rapidly deactivated. Preliminary observation, however, is that solid B at 77°K shows normal phosphorescence in about normal intensity;[18] there is thus no indication of unusual photophysical processes.

The second type of explanation is that the $^4L_1^0$ state is less reactive chemically in B than in A. The rigidity of the cyclam ring might have this effect in a dissociative mechanism, if collapse to a trigonal-bipyramidal intermediate were concerted with loss of the Cl^- ligand. Simple dissociation to a square-pyramidal stage should be equally facile for the two compounds; in fact, the high yield at 254 nm suggests that at this wavelength the mechanism has shifted to one of a nonconcerted heterolytic bond fission. Our results are also explained if $^4L_1^0$ reacts by expanding its coordination sphere to a pentagonal-bipyramidal intermediate by addition of solvent, the unique axis being initially the weak-field one. Solvent would thus be coordinated in the plane perpendicular to this axis; loss of the appropriate ligand with rearrangement of the remaining ligands to an octahedron would yield the products observed in the various cases. A D_{5h} type of intermediate is not unreasonable. It has been pointed out that this geometry is stable relative to the first excited state in O_h on simple crystal-field stabilization grounds.[19] A mechanism of this second type not only allows explanation of stereomobility in photoaquation but now also accounts for the present observations. Compound B, of course, cannot undergo coordination expansion in the plane of the 4 ring. Investigations are continuing on both B and its cis isomer.

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(15) E. Campi, J. Ferguson, and M. L. Tobe, *Inorg. Chem.*, 9, 1781 (1970).

(16) See J. Martin and A. W. Adamson, *Theor. Chim. Acta*, 20, 119 (1971).

(17) S. Chen and G. B. Porter, *Chem. Phys. Lett.*, 6, 41 (1970).

(18) P. Fleischauer, private communication.

(19) A. W. Adamson, *Pure Appl. Chem.*, 20, 25 (1969).

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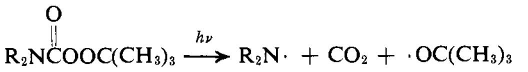
Nitrogen-Centered Free Radicals. III. Formation and Electron Spin Resonance Spectra of *N*-Alkoxy-*N*-alkylamino Free Radicals in Solution[1]

Sir:

In previous work[2] we have shown that dialkylamino free radicals are produced in sufficient quantities in solution for electron spin resonance (esr) studies by photolysis of appropriate 2-tetrazene compounds. As an alternate source of amino radicals we considered the possibility of photodecomposing solutions of *tert*-butyl peroxycarbamates (eq 1 and 2). This method appeared



$$R_2N\overset{\overset{O}{\|}}{C}OOC(CH_3)_3 \xrightarrow{h\nu} R_2N\cdot + CO_2 + \cdot OC(CH_3)_3 \qquad (1)$$

$$RNH\overset{\overset{O}{\|}}{C}OOC(CH_3)_3 \xrightarrow{h\nu} R\dot{N}H + CO_2 + \cdot OC(CH_3)_3 \qquad (2)$$

especially appealing since a variety of alkyl radicals have been observed recently by esr spectroscopy when solutions of *tert*-butyl peresters were photolyzed at reduced temperatures.[3,4]

In contrast to the results with the peresters, we wish to report that only *N*-*tert*-butoxy-*N*-alkylamino radicals were observed by esr spectroscopy when solutions of *tert*-butyl *N*-alkylperoxycarbamates were photolyzed (eq 3). There was no spectral evidence of monoalkylamino radicals. However, irradiation of solu-

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(1) Part II: W. C. Danen and T. T. Kensler, *Tetrahedron Lett.*, 2247 (1971).

(2) W. C. Danen and T. T. Kensler, *J. Amer. Chem. Soc.*, 92, 5235 (1970).

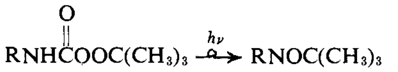
(3) J. K. Kochi and P. J. Krusic, *ibid.*, 91, 3940 (1969).

(4) R. O. C. Norman, Ed., *Chem. Soc., Spec. Publ.*, No. 24, 147 (1970).

Table I. Hyperfine Splitting Constants and *g* Values for *N*-Alkoxy-*N*-alkylamino Radicals[a]

Radical	a^N	$a_\beta{}^H$	$a_{OCH_2R}{}^H$	*g* value[b]	Temp, °C	Method[c]
$CH_3\dot{N}OC(CH_3)_3$	14.47	21.51		2.0048	−90	A (−30°), B, C
$CH_3CH_2\dot{N}OC(CH_3)_3$	14.26	21.23		2.0048	+20	A, B
	14.27	23.37			−80	B–D
	14.28	24.95			−120	B
$CH_3\dot{N}OCH_3$	14.30	21.85	2.62 (R = H)	2.0048	−90	B
$CH_3CH_2\dot{N}OCH_3$	14.00	24.20	2.62 (R = H)	2.0048	−90	B
$CH_3CH_2\dot{N}OCH_2CH_3$	14.31	24.30	2.50 (R = CH_3)	2.0048	−90	B, C

[a] Hyperfine splitting constants and *g* values relative to Fremy's salt taken as 13.091 G and 2.0055, respectively (R. J. Faber and G. K. Fraenkel, *J. Chem. Phys.*, **47**, 2462 (1967); J. Q. Adams and J. R. Thomas, *ibid.*, **39**, 1904 (1964)). Estimated a^N accuracy ±0.4%; β-H hfsc accuracy ±0.8% due to moderate temperature dependency. [b] Corrected for second-order effects; estimated accuracy ±0.0001. [c] Method of generation of radicals: A, photolysis of *ca.* 10% *tert*-butyl peroxycarbamate in benzene or benzene–cyclopropane; B, photolysis of RNHOR′ with di-*tert*-butyl peroxide in cyclopropane; C, photolysis of RNHOR′ in cyclopropane; D, photolysis of RNHOR′ with azomethane in cyclopropane.



$$RNH\overset{O}{\overset{\|}{C}}OOC(CH_3)_3 \xrightarrow{h\nu} R\dot{N}OC(CH_3)_3 \qquad (3)$$

tions of several *tert*-butyl *N,N*-dialkylperoxycarbamates produced weak spectra of the corresponding dialkylamino radicals (eq 1) indicating that the primary photochemical process in the irradiation of peroxycarbamates probably involves formation of amino radicals. The hyperfine splitting constants and *g* values of a number of *N*-alkoxy-*N*-alkylamino radicals are reported in Table I; representative spectra are shown in Figure 1.

The identity of the radicals was ascertained by generating them independently from the corresponding *N,O*-dialkylhydroxylamines either by direct photolysis or by photolysis in the presence of di-*tert*-butyl peroxide or azomethane. Even though photolysis of *N,O*-dialkylhydroxylamines produced *N*-alkoxy-*N*-alkylamino

$$RNHOR' \xrightarrow{h\nu} R\dot{N}OR' \qquad (4)$$

$$RNHOR' \xrightarrow{X\cdot} R\dot{N}OR' + XH \qquad (5)$$
$$X\cdot = (CH_3)_3CO\cdot \text{ or } CH_3\cdot$$

radicals, addition of di-*tert*-butyl peroxide or azomethane increased the intensity of the observed spectra. Also, the methyl radical was not observed in the presence of *N,O*-dialkylhydroxylamines with azomethane whereas a strong signal due to methyl radical was observed in the absence of the hydroxylamine under otherwise identical conditions. Esr spectra of an *N*-alkoxy-*N*-alkylamino radical derived by any of the above methods were identical under identical experimental conditions.[5]

A notable feature of the *N,O*-dialkylhydroxylamines is that the N–H bond is apparently more activated to hydrogen abstraction by an adjacent oxygen than is a C–H bond adjacent to an oxygen or nitrogen. This feature is illustrated by the fact that only nitrogen-centered radicals are observed during the photolysis of RNHOR′ (R = Me, Et; R′ = Me, Et, *tert*-Bu) in the presence of di-*tert*-butyl peroxide in cyclopropane solution (eq 5). It is also apparent from the difference in the methyl group hyperfine interaction between the dimethylamino radical (27.36 G)[2] and the *N*-*tert*-butoxy-*N*-methylamino radical (21.6 G) that the alkoxy substituent group is quite effective in removing spin density from the nitrogen atom. A $\Delta(X_i)$ value[6] of 0.27 can be tentatively assigned to an alkoxy group attached to a nitrogen-centered radical which can be compared with a value of only 0.17 for an alkoxy substituent on a carbon radical. The larger $\Delta(X_i)$ value for the nitrogen-centered radical is reasonable since the greater electronegativity of nitrogen compared to carbon is more effective at stabilizing the charge-separated resonance structure accounting for unpaired electron delocalization.

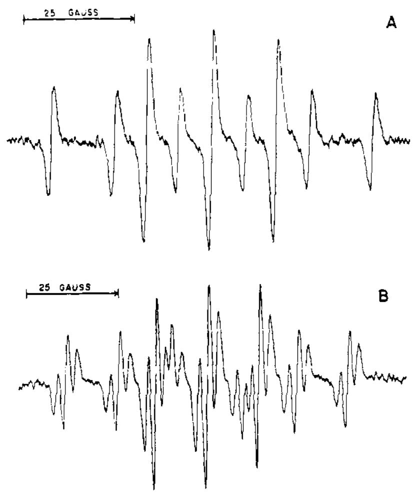


Figure 1. (A) Esr spectrum of the *N*-*tert*-butoxy-*N*-ethylamino radical in cyclopropane at −20° produced by irradiation of *tert*-butyl *N*-ethylperoxycarbamate with a focused 2000-W mercury capillary lamp.[2] (B) Esr spectrum of the *N*-ethoxy-*N*-ethylamino radical in cyclopropane at −90° produced by irradiation of *N,O*-diethylhydroxylamine with di-*tert*-butyl peroxide.

INDO calculations[7] predict a trans coplanar structure for the *N*-methoxy-*N*-methylamino radical and yield $a^N = +11.3$ G, $a_\beta{}^H = +23.6$ G, and $a_\gamma{}^H = +0.5$ G in reasonable agreement with experiment. The spin densities in the nitrogen 2s and 2p orbitals for the structure depicted are calculated to be 0.0299 and 0.7789, respectively; the $\Delta(X_i)$ parameter calculated

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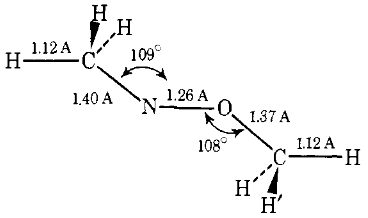
(5) The observation of clean, strong esr spectra of *N*-*tert*-butoxy-*N*-alkylamino radicals in the photodecomposition of *tert*-butyl peroxycarbamates apparently requires a rather efficient formation of the N–O bond. It must be borne in mind, however, that the esr spectrometer detects only those paramagnetic species in adequate concentration under the experimental conditions and that these species may or may not be produced in a major reaction pathway.

(6) $\Delta(X_i)$ is an empirical parameter describing the ability of a substituent to remove spin density from a carbon radical: H. Fischer, *Z. Naturforsch. A*, 20, 428 (1965). The applicability of this type of treatment to a nitrogen-centered radical has not been verified.

(7) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Amer. Chem. Soc.*, 90, 4201 (1968).



above would suggest a lower value than calculated for the 2p orbital.

Preliminary evidence suggests the formation of *N-tert*-butoxy-*N*-arylamino radicals in the decomposition of *tert*-butyl *N*-arylperoxycarbamates. Studies are continuing in this area.

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Primary Kinetic Isotope Effects and the Nature of Hydrogen-Transfer Transition States. The Reaction of a Series of Free Radicals with Thiols

Sir:

The magnitude of the primary isotope effect in a hydrogen-transfer reaction varies with the symmetry of the transition state and is a maximum when the hydrogen is symmetrically bonded to the atoms between which it is being transferred.[1–7] The first indication that such a maximum could be experimentally observed was reported by Kresge[3] and by Bell,[4] who compiled data on proton exchange reactions. In addition, calculations of isotope effects for simplified models of proton transfer reactions are consistent with the conclusion that the isotope effect should pass through a maximum for a symmetrical transition state.[6] Nevertheless, some reservations have been expressed to this hypothesis.[2]

We here wish to report a maximum in the isotope effect for a homologous series of hydrogen-atom transfer reactions. The reactions we have studied involve the abstraction of a hydrogen atom from the S–H position of an isotopically labeled thiol, as shown in eq 1 and 2

$$\mathrm{Q}\cdot + \mathrm{RSH}^* \longrightarrow \mathrm{QH}^* + \mathrm{RS}\cdot \tag{1}$$

$$\mathrm{Q}\cdot + \mathrm{PhSH}^* \longrightarrow \mathrm{QH}^* + \mathrm{PhS}\cdot \tag{2}$$

where Q· is any organic free radical, RSH* is an isotopically labeled aliphatic thiol (usually *tert*-butyl mercaptan), and PhSH* is labeled thiophenol.[8] The postulate, which was first formalized by Hammond,[9,10] suggests that the most symmetrical transition state in such a series of reactions should occur for that case in which the heat of reaction is most nearly zero; exothermic and endothermic reactions would be predicted to have relatively unsymmetrical transition states resembling either reactants or products, respectively. Table I gives the observed isotope effect for a number of organic radicals, the preexponential ratios, and activation energy differences calculated from measurements of the isotope effect as a function of temperature, and a tabulation of the ΔH for each reaction as calculated from bond dissociation energies. Figure 1 shows the relation between the isotope effect and heat of reaction for eq 1 and 2; the curve shows a clear maximum.

Most of the data were obtained using *tert*-butyl mercaptan as RSH* in eq 1. With the exception of the points for the cyclohexyl and 1-adamantyl radicals, all of the data for this mercaptan fall near the curve in Figure 1. Both the cyclohexyl and 1-adamantyl radicals appear to be more reactive than would be predicted from the curve; this greater reactivity is consistent with the notion of some degree of geometrical destabilization for radical centers that may not achieve a planar conformation.[11]

Figure 1 also shows the data for thiophenol as the hydrogen donor, and the data appear to be correlated reasonably well by the same curve that fits the data for the aliphatic thiol. This would be expected since, to a first approximation, the differences in the S–H vibrational frequencies between the thiol and transition state will not be affected by the alkyl or aryl substituent on the sulfur.[12]

The heat of reaction for any given radical is 13 kcal/mol more exothermic for reaction with thiophenol than with *tert*-butyl mercaptan. The isotope effect

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(1) The original postulate and theoretical background for this statement can be found in: (a) F. H. Westheimer, *Chem. Rev.*, **61**, 265 (1961); (b) J. Bigeleisen, *Pure Appl. Chem.*, 8, 217 (1964); (c) L. Melander, "Isotope Effects on Reaction Rates," Ronald Press, New York, N. Y., 1960.

(2) Reservations to this postulate have been expressed by: (a) A. V. Willi and M. Wolfsberg, *Chem. Ind.* (*London*), 2097 (1964); (b) R. F. W. Bader, *Can. J. Chem.*, **42**, 1822 (1964); (c) W. H. Saunders, Jr., *J. Amer. Chem. Soc.*, **91**, 16 (1969); (d) F. G. Bordwell and W. J. Boyle, Jr., *ibid.*, **93**, 512 (1971).

(3) A. J. Kresge, *Discuss. Faraday Soc.*, **39**, 49 (1965).

(4) R. P. Bell has published experimental and theoretical arguments supporting this statement: (a) R. P. Bell, *ibid.*, **39**, 49 (1965); (b) R. P. Bell *ibid.*, **39**, 16 (1965); (c) R. P. Bell and J. E. Crooks, *Proc. Roy. Soc., Ser. A*, **286**, 285 (1965); (d) R. P. Bell and D. M. Goodall, *ibid.*, *Ser. A*, **294**, 273 (1966); (e) D. J. Barnes and R. P. Bell, *ibid.*, *Ser. A*, **318**, 441 (1970); (f) R. P. Bell and B. G. Cox, *J. Chem. Soc. B*, 194 (1970).

(5) For additional experimental work and reviews on this topic see: (a) E. R. Thornton, *J. Org. Chem.*, **27**, 1943 (1962); (b) J. L. Longridge and F. A. Long, *J. Amer. Chem. Soc.*, **89**, 1292 (1967); (c) L. C. Gruen and F. A. Long, *ibid.*, **89**, 1287 (1967); (d) Y. Pocker and J. H. Exner, *ibid.*, **90**, 6764 (1968); (e) A. J. Kresge, D. S. Sagatys, and H. L. Chen, *ibid.*, **90**, 4174 (1968); also, see ref 3; (f) J. E. Dixon and T. C. Bruice, *J. Amer. Chem. Soc.*, **92**, 905 (1970); (g) T. Yokota and R. B. Timmons, *Int. J. Chem. Kinet.*, **2**, 325 (1970); (h) J. R. Jones, *Trans. Faraday Soc.*, **65**, 2138 (1969); (i) J. R. Jones, *ibid.*, **65**, 2430 (1969); (j) J. F. Bunnett, *Surv. Progr. Chem.*, **5**, 53 (1969).

(6) Calculations supporting this postulate are given by: R. A. M. O'Ferrall and J. Kouba, *J. Chem. Soc. B*, 985 (1967).

(7) Since the submission of this paper, several important communications have appeared on this subject: (a) R. P. Bell and B. G. Cox, *J. Chem. Soc. B*, 783 (1971); (b) H. Kwart and M. C. Latimore, *J. Amer. Chem. Soc.*, **93**, 3770 (1971); (c) E. S. Lewis and M. M. Butler, *Chem. Commun.*, submitted for publication, and private communication.

(8) The asterisks in eq 1 and 2 indicate isotopic substitution. Both deuterium and tritium have been used. When tritium is used, the isotope is present in tracer amounts; when deuterium is used, either competition in a mixture of RSH–RSD was used, or parallel experiments were done with normal thiol and then with completely labeled thiol-*S*-d_1.

(9) G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 334 (1955).

(10) For the application to free-radical reactions, see W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966, p 156.

(11) (a) F. D. Greene, C. Chu, and J. Walia, *J. Amer. Chem. Soc.*, **84**, 2463 (1962); (b) J. P. Lorand, S. D. Chodroff, and R. W. Wallace, *ibid.*, **90**, 5266 (1968).

(12) Most thiols have an S–H stretching vibration between 2600 and 2500 cm^{-1}; for example, L. J. Bellamy in "Organic Sulfur Compounds," Vol. I, N. Kharasch, Ed., Pergamon Press, New York, N. Y., 1961, p 51.