Reaction of Triplet Benzophenone with Hydroxylamines: Yields of Radicals and Kinetics of Their Formation and Decay

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Yields of ketyl radicals, $\phi_{KH\cdot}$, triplet-donor reaction rate constants, k_{ir}, and radical decay rate constants, k_{rd}, have been obtained in laser flash irradiation of benzophenone with substituted hydroxylamines in benzene and are, respectively, as follows for the donors studied: $(C_2H_5)_2NOH$, 0.95, 2.1×10^9 M^{-1} s^{-1}, 5.2×10^9 M^{-1} s^{-1}; CH_3NHOCH_3, 0.96, 3.1×10^9, 4.0×10^9; H_2NOCH_3, 1.0, 2.6×10^8, 2.2×10^9; $(CH_3)_2NOCH_3$, 0.30, 1.8×10^8, 1.5×10^9. The reactions proceed (i) via abstraction of H from OH or NH where present and (ii) via initial charge transfer at N in the absence of OH or NH. The very high reaction rates for H atom abstraction from OH or NH are related to the weakening of these bonds by heteroatom resonance stabilization of the O and N centered radicals being formed. The ionization potentials are discussed: O raises IP at adjacent N, N lowers that at O, and alkyl groups lower IP's at both.

Introduction

The linking of nitrogen and oxygen atoms in hydroxylamines weakens both O–H and N–H bonds. The N–H bond energy in *N,O*-di-*tert*-butylhydroxylamine is 81 kcal/mol, compared with 92 in secondary amines, and OH strength in *N,N*-di-*tert*-butylhydroxylamine decreases even further, to 70 kcal/mol from 104 kcal/mol in alcohols.[1,2] Thus, hydroxylamines are readily oxidized to form O-centered and N-centered free radicals. Hydroxylamine itself reacts with ceric ion, giving $NH_2O^\bullet$ and with hydroxyl radical to form $^\bullet$NHOH.[3] The very high reactivity of *N,N*-dialkylhydroxylamines toward alkoxy radicals, leading to nitroxide radicals, has been noted,[4] with rate constants $>7 \times 10^7$ M^{-1} s^{-1}[5] for reaction with *tert*-butoxy radical or ceric ion.[6] Similarly, mono-*N*-alkylnitroxide radicals are formed in reaction of mono-*N*-alkylhydroxylamines with *tert*-butoxyl,[7] and N-centered radicals are readily formed in reactions of *O*-alkyl and *O,N*-dialkylhydroxylamines with methyl[8] or *tert*-butoxyl radical.[9] Formation of C-centered radicals by abstraction of α-CH, activated in the same way by adjacent N or O as in amines and alcohols,[10] may also be expected. *N,N*-Diethylhydroxylamine is an efficient quencher of excited singlet and triplet states of various carbonyl compounds, largely aliphatic.[11] We now report results of a laser flash photolysis study of reactions of photoexcited benzophenone with O- and N-alkyl-substituted hydroxylamines, giving triplet-reductant reaction rate constants and yields and decay rates of the ketyl radicals so formed. The reaction rate constants for H-atom transfers from O and N are very high despite the high ionization potentials of the donors and may be ascribed to weak N–H and O–H bonds rather than to charge-transfer contributions.

Materials and Methods

Benzophenone (Fisher) was recrystallized from ethanol, mp 49–50 °C. *O*-Methylhydroxylamine hydrochloride (Eastman) and *N,O*-dimethylhydroxylamine hydrochloride (Aldrich) were recrystallized from ethanol–ether, mp 149–151 and 112–115 °C, respectively. *N,N,O*-Trimethylhydroxylamine hydrochloride was prepared from *N,O*-dimethylhydroxylamine and methyl iodide, treatment with potassium carbonate, distillation, and addition of hydrogen chloride, mp 118–120 °C.[12] The free bases were obtained by treatment with potassium hydroxide and distillation.[13] *N,N*-Diethylhydroxylamine (Aldrich) was distilled under nitrogen. Benzhydrol was zone refined. Spectral-grade benzene (Eastman) was distilled; acetonitrile (Burdick and Jackson) was used as received; water was triply distilled.

Aliquots, 4 mL, of solutions of benzophenone with the hydroxylamines in desired concentrations were taken in photolysis (1-cm square Pyrex tubes), degassed on a high-vacuum line in three or four freeze–thaw cycles, and left under atmospheric pressure of pure argon or nitrogen. The solutions were subjected to pulsed-laser photolysis at 347 nm using a frequency-doubled ruby laser, as described earlier.[14] Decay of the benzophenone triplet was monitored at 530 nm while the ketyl radical decay was observed at 545 nm.[15]

Under the conditions of this study, the decay of the triplet is pseudo-first order:

$$-\frac{d(\Delta D_T)}{dt} = (k_d{}^0 + k_{ir}[\text{hydroxylamine}])\Delta D_T$$

and the interaction rate constant, k_{ir}, is obtained from the slope of linear plots of the effective first-order rate constant vs donor concentration.

At 530 nm, the triplet absorbs somewhat more strongly than the long-lived ketyl radical, so that both transients can be observed conveniently at this wavelength.[16] Quantum yields of ketyl radical, $\phi_{KH\cdot}$, were obtained, as in previous work,[16] by comparison with reduction of benzophenone triplet by benzhydrol in benzene, for which $\phi_R = 2.0$.[17] Thus, $\phi_R = 2(r_{HA}/r_{BZ})$ where $r = \Delta D_R{}^\infty/\Delta D_T{}^0$, $\Delta D_T{}^0$ is the initial change in absorbance corresponding to triplet formation and $\Delta D_R{}^\infty$ is the absorbance change for the long-lived radical, extrapolated back to $t = 0$.[18] The

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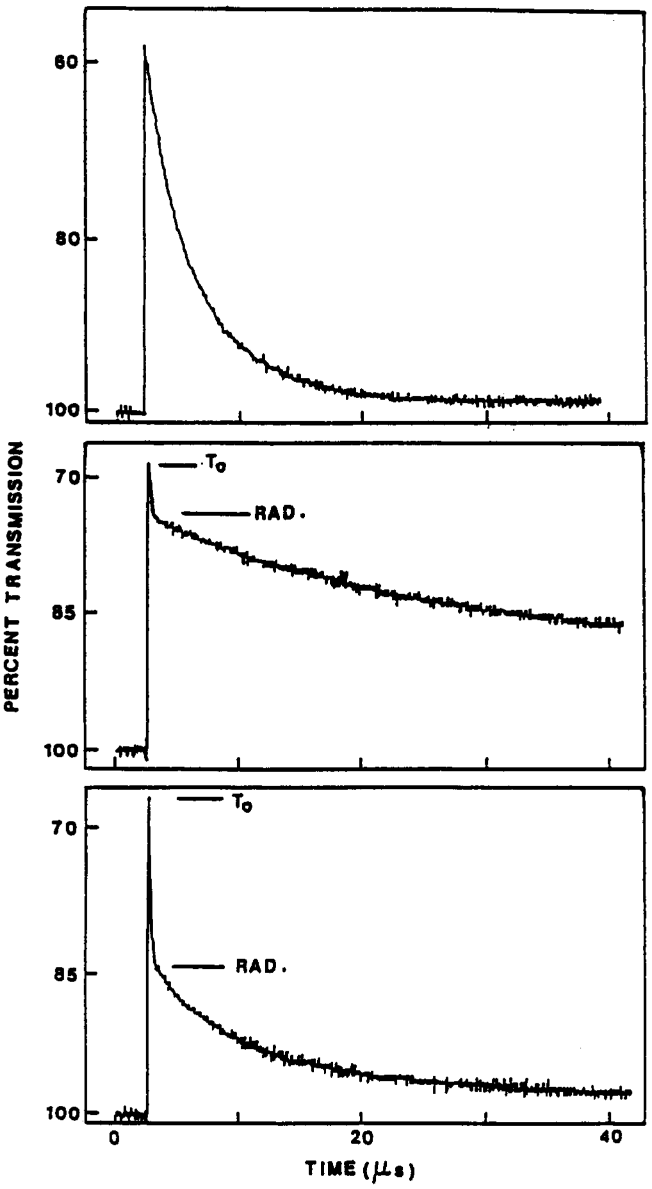

Figure 1. Transmittance (530 nm) vs time following laser flash excitation (347 nm) of 0.004 M benzophenone in benzene: upper oscillogram, without donor; middle oscillogram, with 0.6 M benzhydrol; lower oscillogram: with 0.002 M *N,N*-diethylhydroxylamine. Transmittance of initial triplet and total radical as indicated.

subscripts HA and BZ refer to these ratios for hydroxylamine and benzhydrol respectively. Donor concentrations were adjusted to trap at least 90% of initial triplets, and small corrections to *r* were made for residual unreacted triplet. Figure 1 gives representative data illustrating this technique.

Results

The systems studied were benzophenone with *O*-methylhydroxylamine, *N,O*-dimethylhydroxylamine, *N,N*-diethylhydroxylamine, and *N,N,O*-trimethylhydroxylamine. Figure 2 shows the variation of the effective first-order triplet decay rate constants with donor concentration, from which are obtained the values of $k_d{}^0$ and k_{ir} given in Table I. High values, $k_{ir} > 10^9$ M^{-1} s^{-1}, were observed for *N,N*-diethyl- and *N,O*-dimethylhydroxylamine in benzene, and somewhat lower values, $\geq 10^8$ M^{-1} s^{-1}, for *O*-methyl and *N,N,O*-trimethyl derivatives. The rate constants for *N,O*-dimethyl and *O*-methylhydroxylamine in acetonitrile are slightly lower than in benzene. Table I also lists ionization potentials at N and O for the four donors.

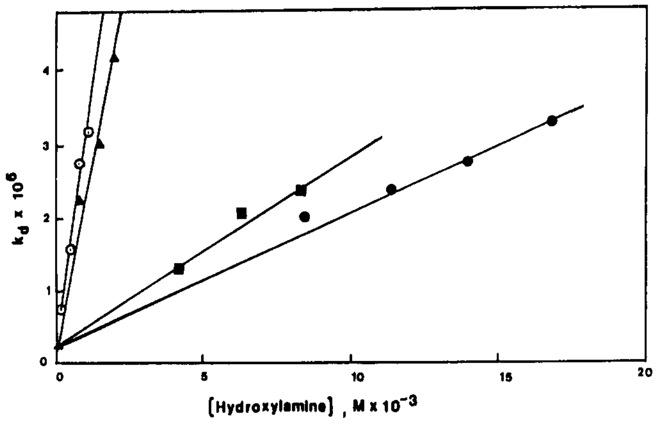

Figure 2. Effective first-order decay constants of benzophenone triplet vs donor concentration: ○, CH_3NHOCH_3; △, $(C_2H_5)_2NOH$; ■, NH_2OCH_3; ●, $(CH_3)_2NOCH_3$.

Table I. Triplet Decay, $k_d{}^0$, and Interaction Rate, k_{ir}, Constants in Benzophenone–Hydroxylamine Systems

hydroxylamine	solvent	$k_d{}^0$ (s^{-1})	k_{ir} (M^{-1} s^{-1})	IP[a] eV N	IP[a] eV O
	C_6H_6	2.5×10^5			
$(C_2H_5)_2NOH$			2.1×10^9[b]	9.2	11.0[c]
CH_3NHOCH_3			3.1×10^9	9.5	10.3
NH_2OCH_3			2.6×10^8	10.2	10.7
$(CH_3)_2NOCH_3$			1.8×10^8	8.1	9.9
	CH_3CN	2.3×10^5			
CH_3NHOCH_3			7.4×10^8		
NH_2OCH_3			1.0×10^8		

[a] Vertical ionization potentials from N and O, taken from ref 19. [b] 1.7×10^9 M^{-1} s^{-1}, reported in ref 11. [c] For $(CH_3)_2NOH$.

Table II. Ketyl Radical Yields and Bimolecular Decay Rate Constants for Benzophenone–Hydroxylamines in Benzene

hydrogen donor	radical quantum yield	k_{rd}/ϵ	k_{rd} (M^{-1} s^{-1})
$(C_6H_5)_2CHOH$[a]	2.00	8.4×10^4	3.6×10^8[b]
$(C_2H_5)_2NOH$	0.95	1.2×10^6	5.2×10^9
CH_3NHOCH_3	0.96	9.2×10^5	4.0×10^9
H_2NOCH_3	1.0[c]	5.1×10^5	2.2×10^9
$(CH_3)_2NOCH_3$	0.30	3.4×10^5	1.5×10^9

[a] Used as reference. [b] For recombination reaction. [c] $\phi_{ketyl} = 0.90$ was obtained in acetonitrile, in a single experiment.

Quantum yields of ketyl radicals were essentially 1.0 in reactions with *N,N*-diethyl-, *N,O*-dimethyl-, and *O*-methylhydroxylamines, which contain either O–H or N–H bonds, but lower, 0.30, with *N,N,O*-trimethylhydroxylamine, which lacks these functions (Table II).

The kinetics of ketyl radical decay were second order in all cases, as shown by linear plots of $\Delta D_R{}^{-1}$ vs time, over at least 2 half-lives (Figure 3). Rate constants derived from the slopes (k/ϵ) of these plots, using $\epsilon = 4340$ M^{-1} cm^{-1},[20] are given in Table II.

For ketyl itself, formed by benzhydrol reduction, the value 3.6×10^8 M^{-1} s^{-1} agrees with previous measurements.[16,20] However, much higher second-order rates are observed with the hydroxylamine donors. In these cases,

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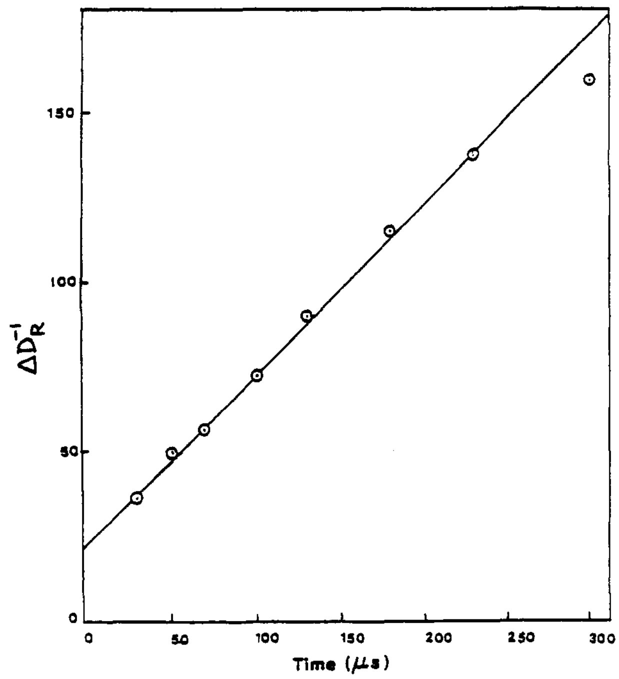

Figure 3. Plot of ΔD_R^{-1} vs time after flashing: 0.004 M benzophenone + 0.01 M NH_2OCH_3 in benzene; λ = 545 nm.

ketyl must disappear preferentially by reaction with stoichiometrically equivalent hydroxylamine-derived radicals rather then with itself.

Discussion

Inverse linear relationships between log k_{ir} and donor IP's have been observed in several systems, with varied donor structures.[21,22] Thus, in reactions of benzophenone triplet with aliphatic amines, k_{ir} increases from ~3 × 10^8 M^{-1} s^{-1} for primary amines to ~3 × 10^9 M^{-1} s^{-1} for secondary and tertiary,[16] while donor IP's decrease from 8.7 to 7.8 and 7.5 eV, respectively.[23] Such correlations indicate that extensive charge-transfer interactions are involved in the primary excited reaction complex.[21] Indeed, the appearance of very high k_{ir} values, close to diffusion controlled, is itself taken as evidence for such interactions.[24] Nevertheless, reduction by hydroxylamines also exhibit high values of k_{ir}, similar to those for amines, although the IP's are much greater (Table I). Such a divergence has also been observed with thioethers as donors.[25]

In hydroxylamines, binding of electronegative O to N exerts strong electron withdrawal, reducing the basicity to pK_a values of 4–6,[13] compared to 9–11 for amines,[26] and markedly raising the ionization potentials at nitrogen, Table I. Hydroxyl and methoxyl groups in $(CH_3)_2NOH$ and $(CH_3)_2NOCH_3$ make the nitrogen IP's 1.4 and 0.3 eV, respectively, higher than 7.8 eV for $(CH_3)_2NH$. On the other hand, NH_2–, CH_3NH–, and $(CH_3)_2N$– in NH_2OCH_3, CH_3NHOCH_3, and $(CH_3)_2NOCH_3$ lower IP's at O by 0.1, 0.5, and 0.9 eV, respectively, below 10.8 eV for methanol. Electron donation by the methyl substituents is marked, and the radical cation formed by abstraction of an electron from either O or N is resonance stabilized, I.

I I

The contribution from O to stabilization of the transition state in abstraction from N is insufficient to fully compensate the effect of the high electronegativity of O; the contribution to stabilization from less electronegative N in abstraction from O overcomes the effect of the electronegativity of N, but in both cases the IP's remain higher than in amines.

However, IP values are not the dominant factors in reaction of the carbonyl triplet with hydroxylamines which contain N–H and O–H functions. Despite high IP's, comparable to that of alcohols, these reactions occur with near-diffusion-controlled rates and with unit quantum yields of ketyl, apparently largely via direct abstraction of H from N or O. These processes are greatly facilitated by resonance stabilization of the developing N- or O-centered radicals by the adjacent heteroatom, as indicated by

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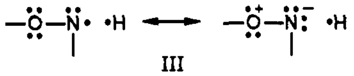

III III

and accounting for the low dissociation energies of these bonds in hydroxylamines. Charge development and delocalization in these radical stabilizations and the relative electronegativities of the two heteroatoms lead to the observed greater weakening of the normally stronger O–H bond. The lower value of k_{ir} for NH_2OCH_3 than for CH_3NHOCH_3 may arise from a higher bond energy in $-NH_2$ than in CH_3NH–.[8] The similar values of k_{ir} in acetonitrile and in benzene are consistent with reactions proceeding via initial attack at –H rather than by initial charge transfer. The relatively low basicity of the hydroxylamines is also in accord with a greater tendency than in amines for proton movement to accompany electron transfer to the acceptor triplet. Generally similar considerations involving redox potentials, bond strengths, and basicities have been proposed to account for differences in the reactions of formate ion with triplets of benzophenone (H atom transfer) and anthraquinone (electron transfer).[27]

N,N,O-Trimethylhydroxylamine, which has the lowest IP, but contains no NH or OH, shows lowest k_{ir} and low $\phi_{KH\cdot}$, 0.30, compared with unity for the other cases. Its IP is close to those of the aliphatic amines, and like those, its reaction may well start via charge transfer at N. In this case, resonance stabilization, as in I, apparently results in back-electron transfer and partial quenching and diminished efficiency in abstraction of H from α-C, compared with unity efficiency with aliphatic amines including tertiary amines.[16] In this respect the trisubstituted hydroxylamine resembles the thioethers, thioanisole, and di-*n*-butyl sulfide, which give low ketyl quantum yields, 0.35 and 0.13, respectively, and have comparatively high values of k_{ir}, 9.3 × 10^7 and 9 × 10^8 M^{-1} s^{-1}, and high IP's, 8.9 and 8.4 eV.[25]

As has been reported,[5] heteroatom-centered radicals derived from hydroxylamines may be effective traps for C-centered radicals. Formed in these systems by hydrogen

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abstraction from N or O, they react with diphenylketyl more rapidly than the bulky resonance-stabilized ketyl radicals dimerize, Table II. C-Centered radicals formed from the *N,N,O*-trimethyl compound, and possibly in part from the others, are less stabilized and bulky than the ketyl, and would also increase rates of removal of ketyl.

Although the N- and O-centered radicals react very rapidly with ketyl radicals, they may not react rapidly alone. Nitroxide radicals from *N,N*-dialkylhydroxylamines may appear stable, in equilibrium with their dimers,[28] or they may disproportionate by slow transfer of H from α-C with rate constants $\sim 10^3$ M^{-1} s^{-1}.[6] Mono-*N*-alkylnitroxide radicals disproportionate more rapidly, with transfer of H from N and rate constants $>10^6$ M^{-1} s^{-1}.[7] *O,N*-Dialkyl- and *O*-monoalkyl N-centered radicals disappear more rapidly, apparently by initial dimerization, with rate constants $\sim 10^8$ M^{-1} s^{-1},[29] similar to that for diphenylketyl dimerization. In this study, reactions of the hydroxylamine-derived radicals with ketyl radical dominate over these self-destruction processes.

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Registry No. Benzophenone, 119-61-9; *O*-methylhydroxylamine, 67-62-9; *N,O*-dimethylhydroxylamine, 1117-97-1; *N,N*-diethylhydroxylamine, 3710-84-7; *N,N,O*-trimethylhydroxylamine, 5669-39-6; benzophenone ketyl radical, 16592-08-8.

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Molecular Recognition of Polar Neutral Molecules by Metallomacrocycles: Synthesis, ^{1}H NMR Spectroscopy, X-ray Structure, Electrochemistry, and Ab Initio Calculations

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*Metallo*macrocycles **5** possessing an immobilized Lewis acidic uranyl group were synthesized by reaction of aldehydes **4** with *cis*-1,2-cyclohexanediamine in the presence of Ba^{2+} as a template cation and subsequent transmetallation with UO_2^{2+}. These metallomacrocycles are soluble in organic solvents and the complexation with neutral molecules was investigated by polarography, ^{1}H NMR spectroscopy, solid–liquid and liquid–liquid extraction experiments, X-ray structure determinations, and ab initio calculations. Several solid complexes (**6**) of metallomacrocycles **5b–d** with polar neutral molecules (formamide, acetamide, *N*-methylurea, hydroxyurea, urea, and DMSO) were isolated; a ring size selective complexation is observed. Polarography demonstrated a ring size affinity with the following stability order for the complexes in CH_3CN: urea > *N*-methylurea > acetamide ≈ formamide > acetone ≈ 0. The stability constants of the **6b**·urea and **6c**·urea complexes in $CDCl_3$ are according to ^{1}H NMR spectroscopy at least 10^5 M^{-1}; the highest number ever achieved by a complex consisting of a neutral *mono*metalloreceptor and a neutral molecule. The high stabilities were confirmed by solid–liquid and liquid–liquid extraction experiments. The crystal structures of the **6b**·urea and **6d**·urea complexes reveal that urea is encapsulated in the cavity and that the complexes are stabilized by coordination of the carbonyl oxygen of urea to the immobilized uranyl cation, multiple H-bond formation, and electrostatic interactions between urea nitrogens and ether oxygens. Ab initio calculations suggest that charge transfer determines the coordination between the uranyl cation and urea. The optimal coordination angle ($C{=}O{\cdots}M^{2+}$) is approximately 130°, for both in-plane and perpendicular coordination.

Introduction

In supramolecular chemistry one of the major objectives is the selective complexation of *neutral guests*. The first generation of receptors for neutral molecules were relative simple and have only a moderate preorganization and complementarity between host and guest. The recognition of these receptors is based on H-bond formation of the acidic protons of the guest and the Lewis basic sites (e.g. crown ether oxygens) of the host.[1]

The structure of the second generation receptors is more complex. In the design of this new generation stereoelectronic and size complementarity play an important role. Both π–π stacking and H-bond formation contribute to the stability of these complexes.[2] For achievement higher

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