Quenching of Oxygen($^1\Delta_g$) by Amines

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Abstract: The electronic relaxation of the lowest singlet state of molecular oxygen has been studied in the presence of a number of aliphatic amines. Rate constants have been obtained for quenching by mono-, di-, and trimethyl- and ethylamines and 1,4-diazabicyclo[2.2.2]octane (DABCO). The constants range between 2×10^5 l. mol^{-1} sec^{-1} (for monomethylamine) and 1.9×10^7 l. mol^{-1} sec^{-1} (for triethylamine) and display a good correlation with the ionization energy of the quencher. Temperature and pressure dependency studies indicate that no bound intermediate is formed, and the results can be rationalized in terms of a "contact charge-transfer" interaction.

The possibility that singlet molecular oxygen is involved in a variety of photodynamic processes in the biosphere has been suggested by several authors.[1-3] Efficient quenchers of this species may therefore be of some practical importance. It was recently reported by Ouannès and Wilson[4] that several tertiary aliphatic amines are capable of inhibiting the oxidation of known "singlet oxygen" acceptors while undergoing no permanent change themselves. A qualitative experiment in which 1,4-diazabicyclo[2.2.2]octane was introduced into a stream of singlet oxygen provided direct evidence for efficient quenching of $O_2(^1\Delta_g)$.

Since a number of aliphatic amines are sufficiently volatile at room temperature to be easily introduced into a low-pressure discharge-flow system, the rate constants for the relaxation of $O_2(^1\Delta_g)$ by amines can be determined directly. Earlier studies[5] have established the nature of the species present in the products of a low-pressure discharge in oxygen. When the atoms are removed from the stream by mercury contamination,[6] the stream has a composition that is typically 95% $O_2(^3\Sigma_g^-)$, 5% $O_2(^1\Delta_g)$, and 0.04% $O_2(^1\Sigma_g^+)$. The concentrations of these species do not change much along the length of a typical fast-flow tube because of the great stability of $O_2(^1\Delta_g)$. Though $O_2(^1\Sigma_g^+)$ is efficiently deactivated by a variety of molecules,[7] in a flow system its concentration assumes a steady-state value determined by the reactions

$$2O_2(^1\Delta_g) \longrightarrow O_2(^1\Sigma_g^+) + O_2(^3\Sigma_g^-)$$

$$O_2(^1\Sigma_g^+) + \text{walls} \longrightarrow O_2(^1\Delta_g) + \text{walls}$$

This sequence of reactions does not represent a significant decay mechanism for $O_2(^1\Delta_g)$.[8] For the present study the presence of a small steady-state concentration of $O_2(^1\Sigma_g^+)$ in the stream is of no consequence.

The numerous radiative processes which these excited molecules can participate in include the process[9]

$$2(^1\Delta_g) \longrightarrow 2(^3\Sigma_g^-) + h\nu \text{ (6340 Å)}$$

which does not contribute significantly to the decay process. However, it provides a convenient method of monitoring the concentration of the excited molecules in a flow system.

Experimental Section

The conventional discharge-flow system used in this work is similar to that described earlier.[7,8] It consisted of a Pyrex observation tube 12.5 cm in diameter and 50 cm long. A 50 l./min rotary pump typically produced a linear flow rate of 75 cm/sec and a pressure of 2.25 Torr with an oxygen flow of 93 μmol/sec. These were found to be the most suitable conditions for quenching measurements at room temperature.

Matheson "extra-dry" oxygen and reagent grade amines were used without further purification. $O_2(^1\Delta_g)$ was produced in the oxygen stream with a 100-W 2450-MH discharge. The oxygen atoms were removed from the stream by distilling a small amount of mercury through the discharge.[6]

The concentration of $O_2(^1\Delta_g)$ was monitored by its emission at 6340 Å. Since the band is proportional to the square of the $O_2(^1\Delta_g)$ concentration it provides a very sensitive method of following changes in this species. A Zeiss wedge interference filter was used to isolate the band and also check for the absence of atoms in the stream which give rise to higher energy emission in the presence of NO. The radiation was detected with an RCA-7265 photomultiplier coupled to a Hamner photon counter and recorder. Baffles placed between the photomultiplier and the observation tube limited the segment of the tube under view at any time to about 1 cm.

The flow of amine was determined for each experiment by trapping and weighing the condensate or by following the pressure drop in the storage bulb. The temperature of the observation tube was varied by circulating a hot or cold liquid through a jacket surrounding the tube.

Results

In agreement with the observations of Ouannès and Wilson[4] we could find no evidence for any reaction between $O_2(^1\Delta_g)$ and any of the amines investigated, even when the amine concentration was such that a single molecule was responsible for deactivating more than 10^2 molecules of $O_2(^1\Delta_g)$.

Figure 1 summarizes the data obtained for the decay of $O_2(^1\Delta_g)$ along the observation tube in the absence of added gas (labeled O) and in the presence of increasing amounts of trimethylamine. In all cases the logarithmic plot was found to be linear, suggesting the process is always first order in $O_2(^1\Delta_g)$. In the absence of any added quencher, there is a homogeneous and heterogeneous decay of $O_2(^1\Delta_g)$[5] which can be represented by the equation

$$O_2(^1\Delta_g) \xrightarrow{k_1} O_2(^3\Sigma_g^-)$$

In the presence of a quencher (Q) we have

$$O_2(^1\Delta_g) + Q \xrightarrow{k_Q} O_2(^3\Sigma_g^-) + Q$$

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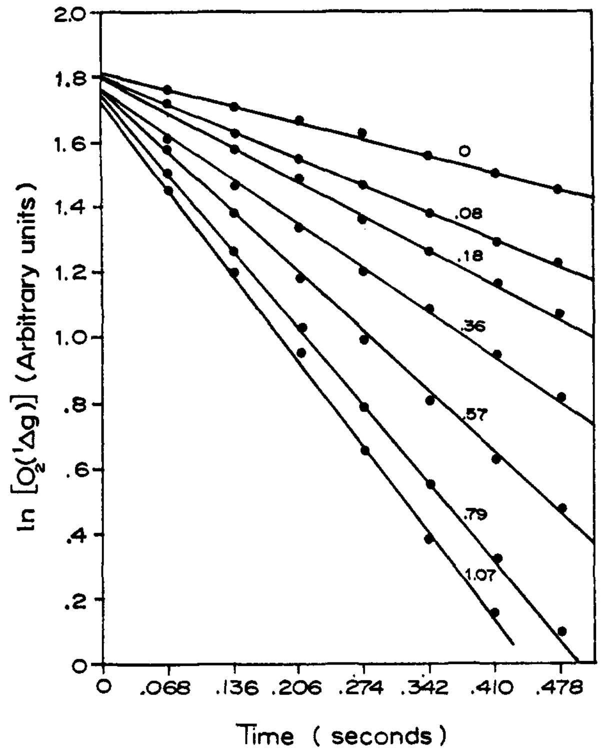

Figure 1. Decay of $O_2(^1\Delta_g)$ as a function of time in the presence of trimethylamine. The concentration of the amine in μmol/l. is indicated above each line.

Hence the time evolution of the system is governed by the relation

$$-\ln [O_2(^1\Delta_g)] = (k_1 + k_2[Q])t + \text{constant}$$

The slopes of the lines in Figure 1 are therefore equal to $-k_1 - k_2[Q]$. In Figure 2 these slopes are plotted against the concentration of trimethylamine. The slope of the line in Figure 2 is equal to k_q. This quenching rate constant together with the quenching constants for several other amines, which were determined in the same manner, are listed in Table I.

Table I. Rate Constants for the Process

$$O_2(^1\Delta_g) + Q \xrightarrow{k_q} O_2(^3\Sigma_g^-) + Q$$

Q	Ionization energy of Q, eV[10]	k_q, l. mol^{-1} sec^{-1}
Monomethylamine	9.4	$2.0 \pm 0.2 \times 10^5$
Dimethylamine	8.9	$6.5 \pm 0.6 \times 10^5$
Trimethylamine	8.3	$3.0 \pm 0.4 \times 10^6$
Monoethylamine	9.2	$3.3 \pm 0.3 \times 10^5$
Diethylamine	8.4	$2.0 \pm 0.2 \times 10^6$
Triethylamine	7.5	$1.9 \pm 0.1 \times 10^7$
DABCO	Unknown	$1.2 \pm 0.1 \times 10^7$

In an attempt to distinguish between "bound" and "collisional" intermediates in the quenching reaction, the quenching by trimethylamine was studied at three different temperatures. The decay of $O_2(^1\Delta_g)$ at 2, 24, and 84° is shown in Figure 3. The broken lines give the decay in the absence of any quencher. The solid lines give the decay in the presence of a flow of 0.43 μmol/sec of trimethylamine. When the flow of amine is fixed, its concentration in the observation tube increases with decreasing temperature because it is governed by the relation $C = P/RT$, and the pressure in the flow system is not measurably changed by a variation in the temperature of the observation tube. Taking into account this concentration change, the rate constants at these three temperatures are: k_q (2°) = 2.2×10^6, k_q (24°) = 2.7×10^6, k_q (84°) = 3.4×10^6 l. mol^{-1} sec^{-1}. The logarithms of these values are plotted as a function of $1/T$ in Figure 4. From the slope of this line we obtain an activation energy of 5.6 ± 0.5 kcal/mol for the quenching reaction.

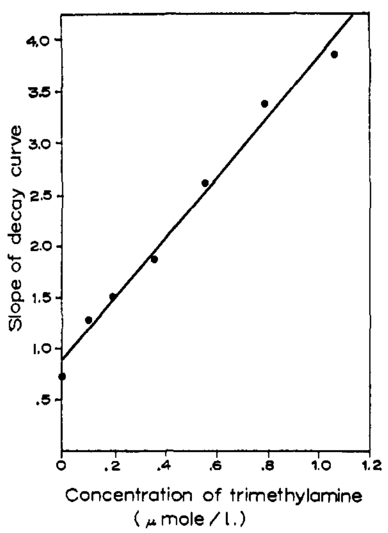

Figure 2. Slopes of the lines in Figure 1 as a function of the concentration of trimethylamine.

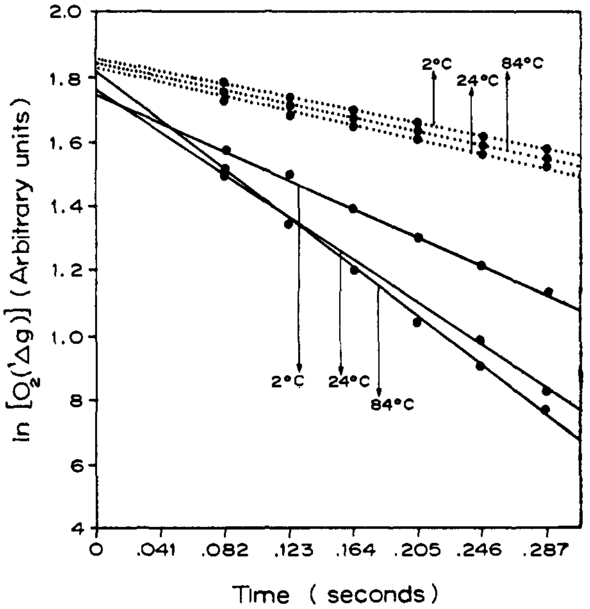

Figure 3. Decay of $O_2(^1\Delta_g)$ at three temperatures in the absence of any quencher (···) and in the presence of 0.43 μmol/sec of trimethylamine (——).

Discussion

Though the quenching rate constants for tertiary amines are greater than the values that have been reported for any other volatile molecule, the largest value is still about 10^4 below collision frequency. In Figure

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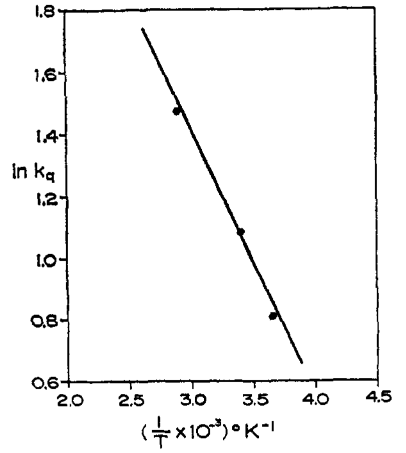

Figure 4. Natural logarithm of the quenching constants for trimethylamine as a function of the reciprocal of the absolute temperature.

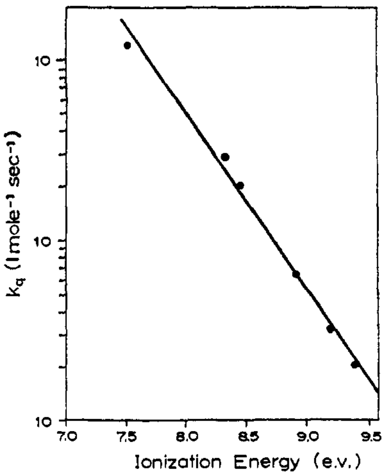

Figure 5. Relationship between the quenching constants for some aliphatic amines and their ionization energies.

5 these rate constants are plotted against the ionization energies of the quencher. The correlation between log k_q and ionization energy is remarkably good for these six amines. It is therefore tempting to interpret the quenching in terms of a "charge-transfer" type interaction[11,12] between $O_2(^1\Delta_g)$ and the amines, in which the amine acts as a donor and the oxygen as acceptor. However, it should be noted that the observed temperature dependence of the quenching constant is consistent with a simple "collisional" process which occurs with greater efficiency when the temperature is higher, *i.e.*, when the interaction energy is greater. It is not consistent with a weakly bound complex which could be in equilibrium with $O_2(^1\Delta_g)$ and amine, nor is the temperature dependency what one would expect for a strongly bound complex.[13]

Earlier experimental and theoretical studies of induced radiationless intersystem crossing have been concerned with either heavy-atom effects[14,15] or the role of paramagnetic species such as O_2 and NO.[16,17] These have little relevance for the present system, since in the process

$$O_2(^1\Delta_g) + \text{amine} \longrightarrow O_2(^3\Sigma_g^-) + \text{amine} + 22.5\ \text{kcal/mol}$$

the perturbing amine is a "singlet" and possesses no heavy atom. However, the following qualitative interpretation seems consistent with the currently popular quantum mechanical view of such phenomena.[18]

The zero-order states for the system are taken to be the simple product of the appropriate unperturbed states of oxygen ($^3\Sigma$ and $^1\Delta$) and the amine (^{1}A). The transition, which can be written $^1[^1\Delta\cdot{}^1A] \rightarrow {}^3[^3\Sigma\cdot{}^1A]$, is formally forbidden because of the singlet–triplet multiplicity change in the complex. To accomplish such a "spin flip" we require an interaction between the spin magnetic moment of an electron and the magnetic moment due to its orbital motion. Though such spin–orbit coupling is normally associated with heavy atoms because it is proportional to the fourth power of the atomic number, it may be that in the present case a relatively small coupling (associated perhaps with the nitrogen atom[19]) is sufficient. The mechanism by which the transition occurs could then be the following. The interaction between the molecular pairs mixes into the above zero-order states some of the excited charge-transfer states. For the initial complex this would be the singlet charge-transfer state (^{1}CT), while for the final system this must be the triplet charge-transfer state (^{3}CT). It is quite likely that these charge-transfer states lie energetically quite close to one another,[11] and because of the charge separation they only formally retain their singlet and triplet character. Consequently, a relatively small spin–orbit coupling would then be able to mix these two charge-transfer states, allowing the spin flip to occur. Such a process is summarized by the equation

$$^1[^1\Delta\cdot{}^1A + \lambda(^1CT)] \xrightarrow[\text{interaction}]{\text{spin–orbit}} {}^3[^3\Sigma\cdot{}^1A + \mu(^3CT)]$$

where λ and μ are a measure of the extent to which the two complexes possess charge-transfer character. Since the extent to which such charge-transfer states are mixed with the neutral states of the complex should be directly related to the ionization energy of the donor,[11] this description is consistent with the correlation found in Figure 5.

Recently Nakajima and Akamatu[20] have reported the quenching of rubicene fluorescence by amines. A similar correlation of quenching rate constant with ionization energy was obtained. In this case it is not known whether internal conversion or intersystem crossing is involved, and hence the relationship of their results to ours is uncertain.

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