

A REDETERMINATION OF THE RATE CONSTANTS FOR THE QUENCHING OF GASEOUS $O_2(^1\Delta_g)$ BY ALIPHATIC AMINES

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SUMMARY

Because some of the earlier determinations of $O_2(^1\Delta_g)$ quenching constants have been shown to be in error due to the presence of oxygen atoms, we have redetermined them under conditions where the absence of atoms can be guaranteed. The values obtained are considerably smaller than those reported previously and the correlation of the quenching constants with the ionization energy of the quencher is not as clear. However, evidence is presented which indicates that the forces responsible for the induced relaxation can still be identified with those commonly classified as "charge-transfer" interactions.

INTRODUCTION

The collision induced relaxation of electronically excited molecules is not yet sufficiently well understood to allow us to predict the quenching abilities of different molecules. The stumbling block appears to be the experimental difficulty of finding a sufficiently large range of suitable quenchers which can be used with a given electronically excited molecule. Some frequent obstacles are the solubilities of the quenchers and the existence of more rapid competitive processes such as chemical reaction, energy transfer or radiative decay¹. The first two electronically excited states of the oxygen molecule: $O_2(^1\Delta_g)$ (at 22.5 kcal) and $O_2(^1\Sigma_g^+)$ (at 37.5 kcal) are remarkably free from these complications. They have long radiative lifetimes, are singularly unreactive, and have extremely limited possibilities for energy transfer. They can readily be obtained in the gas phase by several techniques² and conveniently used for kinetic studies.

In the last few years we have reported quenching rates for both these systems^{3,4}. However, in the case of the spin forbidden process ($^1\Delta_g \rightarrow ^3\Sigma_g^-$) we recently discovered⁵ that for organic quenchers oxygen atoms (present as an "impurity") can lead to anomalously high values for the quenching constants. In

the present study we have therefore repeated our earlier measurements of the quenching constants for aliphatic amines to determine whether the previously reported⁴ correlation of quenching efficiency with the ionization energy of the quencher is correct.

EXPERIMENTAL

The conventional discharge-flow system used in this work was similar to that described earlier³. The observation tube was 1 m long and had an internal diameter of 49 mm. With a suitable throttled 500 l/min pump, a flow of 300 cm/sec was established along the tube for most experiments. A 100 W, 2450 MHz microwave generator was used to produce the singlet oxygen ($^1\Delta_g$) in a stream of "Matheson extra dry" oxygen. Oxygen atoms were removed by slow distillation of mercury through the discharge. The complete absence of oxygen atoms in the stream was assured by the addition of NO_2 just before the observation tube. Sufficient NO_2 was added to guarantee its continuous deposition in the pump-trap; however, its flow was kept at least an order of magnitude smaller than necessary to cause any $\text{O}_2(^1\Delta_g)$ quenching or produce any measurable glow from NO_2^* formed in an energy-pooling reaction with $\text{O}_2(^1\Delta_g)$ ⁶.

The concentration of $\text{O}_2(^1\Delta_g)$ along the observation tube was monitored by following the 6340 Å emission with a movable RCA-7265 photomultiplier coupled to a lock-in amplifier and a digital voltmeter. Rate constants were calculated by taking the difference between the $\text{O}_2(^1\Delta_g)$ decay rates in the presence and absence of the quenching species.

The amines were obtained from Aldrich Chemical Co. and Eastman Chemicals Ltd., and checked for purity by gas chromatography. No further purification was attempted. The flow of each quencher was individually determined by following the pressure drop in a storage vessel of known volume.

RESULTS

In contrast to some of our earlier work⁷, the rate constants for quenching of $\text{O}_2(^1\Delta_g)$ by amines showed no variation when the pressure was varied between 1 and 5 torr. Furthermore, the orders of the reactions with respect to $\text{O}_2(^1\Delta_g)$ and quencher (Q) were both always found to be unity. As we pointed out in a recent communication⁵, the much less reproducible results obtained by earlier workers were probably due to the presence of small concentrations of oxygen atoms which manage to slip past the mercuric oxide surface. In the current study, in which NO_2 was added to the stream in order to guarantee the absence of oxygen atoms no such difficulties arose.

Table I lists the quenching rate constants calculated from our results. The values reported were determined at a total pressure of 3.5 torr where the most

TABLE I
RATE CONSTANTS FOR O₂(¹Δ_g) QUENCHING AT 300 K

Quencher	Ionization energy (eV)	k_q (l mole ⁻¹ sec ⁻¹)	log ₁₀ k_q
Triethylamine	7.50	2.0 (±.1) × 10 ⁶	6.30
Trimethylamine	7.82	1.9 (±.1) × 10 ⁶	6.28
Diethylamine	8.01	7.3 (±.3) × 10 ⁴	4.86
Dimethylamine	8.24	5.6 (±.3) × 10 ⁴	4.75
Ethylamine	8.86	7 (± 1) × 10 ³	3.85
Methylamine	8.97	8 (± 1) × 10 ³	3.9

reliable results were obtainable. The error was estimated from the reproducibility of the decay measurements and the accuracy of the flow and pressure measurements. It will be observed that the error limits are considerably larger for poor quenchers. With our current apparatus smaller quenching rates are more difficult to measure accurately.

DISCUSSION

There are several significant differences between the present values and those reported earlier⁴ when atoms were not completely removed. First the values in Table 1 are all considerably smaller than the earlier ones. We have attributed this to the formation of a very efficient O₂(¹Δ_g) quencher when oxygen atoms react with organic molecules such as amines, olefins and sulfides⁵. Our attempts to identify the quenching species with a mass spectrometer have not been successful and the solution to this particular question will probably require an understanding of the detailed mechanism of these oxygen atom reactions.

Recently Herron and Huie⁸ reported a determination of the quenching constant for O₂(¹Δ_g) by triethylamine. Their value of 2 × 10⁶ l mole⁻¹ sec⁻¹ is in excellent agreement with our current value. The mass spectrometric technique which they used required the presence of another hydrocarbon. This may have removed the effect of atoms if some were present in their system.

The second significant difference in the present results is the less satisfactory correlation of the rate constants with the ionization energy of the quencher. This is illustrated in Fig. 1. It would appear that though the substitution of an alkyl group for a hydrogen atom in an amine greatly affects its quenching ability and ionization energy, the substitution of an ethyl for a methyl group leads to no significant change in the quenching constant even though there is a significant decrease in the ionization energy of the molecule.

These results do not appear to support the previous explanation of induced relaxation in terms of "charge-transfer" interactions⁴. It has always been assumed that for any given acceptor, the magnitude of the interaction in a charge-transfer complex is directly related to the ionization energy of the donor^{9,10}. However

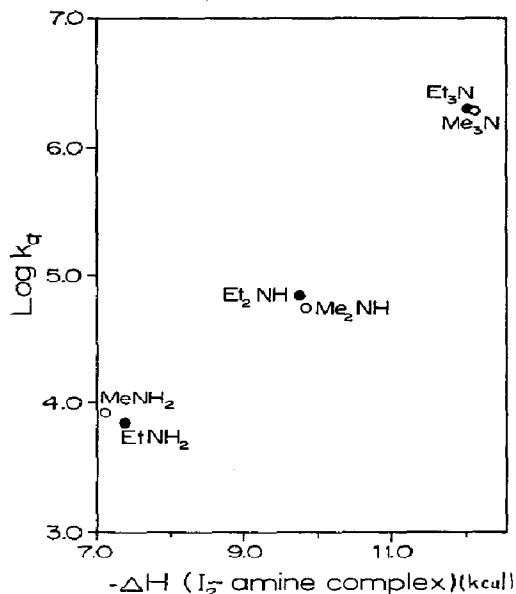
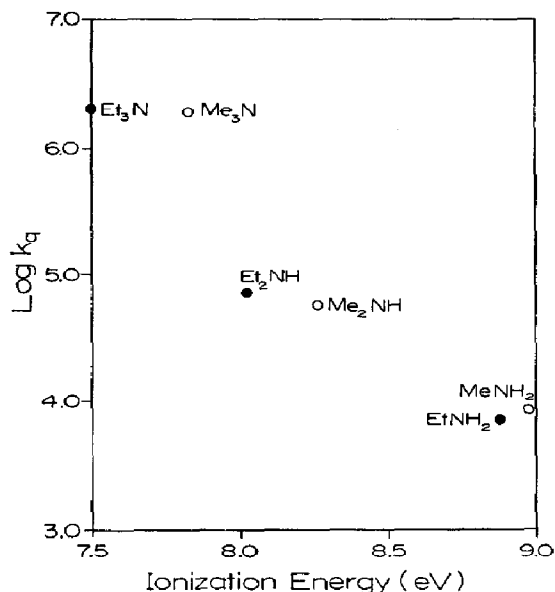


Fig. 1. Logarithm of the rate constant for $O_2(^1\Delta_g)$ quenching by ethyl and methyl amines as a function of the ionization energy of the amine.

Fig. 2. Logarithm of the rate constant for $O_2(^1\Delta_g)$ quenching by ethyl and methyl amines as a function of the dissociation energy (ΔH) of the corresponding I_2 -amine complex.

there exist some data which indicate that the relationship may not be that simple. For example, the work of Yada *et al.*¹¹ on charge-transfer complexes between amines and I_2 yielded values for the dissociation energies shown in Table 2 as ΔH . It can be seen that the ethyl and methyl derivatives form complexes with very similar bond strengths despite their very different ionization energies. In Fig. 2 we have plotted these bond strengths against the logarithm of the $O_2(^1\Delta_g)$ quenching constants obtained in the present work. The correlation is certainly more satisfactory than that found in Fig. 1 and it is probably worth considering a possible theoretical base for such a correlation.

Consider a system composed of a donor (D) and an acceptor (A) which is described by the solid potential energy curves shown in Fig. 3. In the ground state

TABLE 2
DATA ON I_2 -AMINE COMPLEXES¹¹

Amine	$-\Delta H$ (kcal)	I.E. (eV)	$h\nu_{CT}$ (kcal)	$\frac{\Delta H}{h\nu_{CT}}$
Et_3N	12.0	7.50	69.1	0.174
Me_3N	12.1	7.82	69.1	0.175
Et_2NH	9.7	8.01	69.8	0.139
Me_2NH	9.8	8.24	69.5	0.141
$EtNH_2$	7.4	8.86	68.6	0.108
$MeNH_2$	7.1	8.97	68.4	0.104

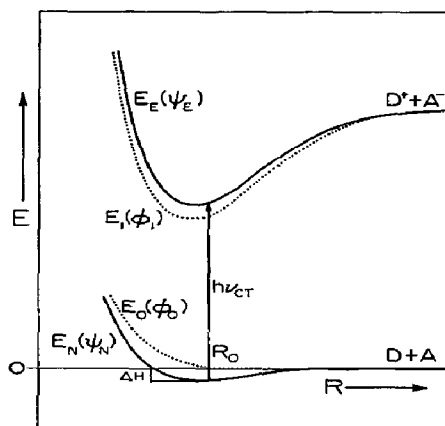


Fig. 3. Solid curves: potential energy curves for the ground state and "charge transfer" state formed between a donor (D) and acceptor (A). Broken curve: theoretical "no bond" state (E_0) and "dative" state (E_1) used in the description of the donor-acceptor interaction.

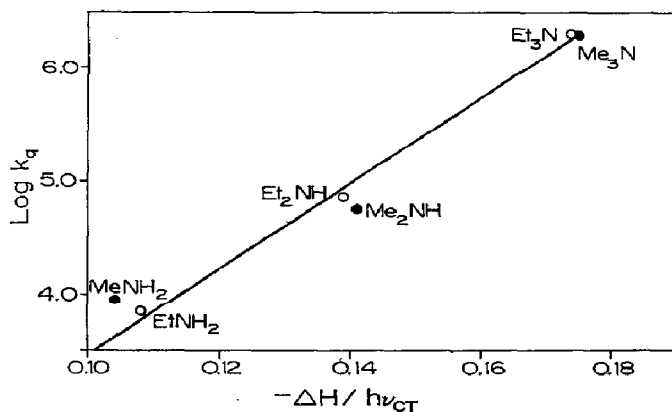


Fig. 4. Logarithm of the O₂(¹Δ_g) quenching constant as a function of the ratio ($\Delta H/h\nu_{CT}$) characteristic of the I₂-amine complexes (see Table 2).

(labelled E_N and characterized by the wave function ψ_N) a weakly bound complex is formed with an equilibrium separation R_0 and a dissociation energy ΔH . An excited charge-transfer state labelled E_E (and characterized by ψ_E) has a dissociation limit given by the difference between the ionization energy of D and the electron affinity of A. A transition to this state from the ground state at R_0 gives rise to a "charge-transfer band" with a maximum at " $h\nu_{CT}$ ".

Mulliken¹² has proposed a description of these states in terms of a "no-bond" function ϕ_0 and a "dative structure" ϕ_1 , shown as dotted curves in Fig. 3. According to this theory the two observable states ψ_N and ψ_E can be described approximately by a linear combination of ϕ_0 and ϕ_1 thus:

$$\psi_N = a\phi_0 + b\phi_1 \text{ and } \psi_E = a\phi_1 - b\phi_0$$

where $a \gg b$. Second order perturbation theory then yields¹¹:

$$b^2/a^2 = (E_N - E_0)/(E_0 - E_1).$$

If it is assumed that at the equilibrium internuclear separation (R_0) of the complex:

$$E_N - E_0 \approx \Delta H \text{ and } E_0 - E_1 \approx h\nu_{CT}$$

$$\therefore b^2/a^2 \approx -\Delta H/h\nu_{CT}.$$

This equation predicts that the coefficient b^2 (which is a measure of the amount of charge-transfer character in the ground state) is proportional to $\Delta H/h\nu_{CT}$. The quantities ΔH , $h\nu_{CT}$ and $\Delta H/h\nu_{CT}$ are listed in Table 2 for some I_2 -amine complexes, and $\Delta H/h\nu_{CT}$ is plotted against $\log k_q$ for $O_2(^1\Delta_g)$ in Fig. 4. It can be seen that the correlation is not significantly different from that in Fig. 2. Since $h\nu_{CT}$ does not vary much in these complexes, not much difference would be expected. The improved linear correlation can be expressed mathematically by calculating¹³ a "sample correlation coefficient" r . The values we obtained with a simple linear regression program are:

$$r = 0.940 \text{ for the correlation with ionization energy}$$

$$r = 0.985 \text{ for the correlation with } \Delta H_{CT}$$

$$r = 0.989 \text{ for the correlation with } \Delta H_{CT}/h\nu$$

The conclusions we would like to draw from the above analysis are the following: (a) the values of ΔH for the I_2 -amine complexes are a reasonable measure of the magnitude of the "charge-transfer" interaction in these complexes; (b) in view of the correlation between the $O_2(^1\Delta_g)$ quenching constants and ΔH for the I_2 -amine complexes, the magnitude of the "charge-transfer" interaction is also the most important factor in determining the $O_2(^1\Delta_g)$ quenching rates with amines. It will be noted that the magnitudes of the $O_2(^1\Delta_g)$ quenching constants and the lack of a pressure dependence indicate the interactions are very much weaker between $O_2(^1\Delta_g)$ and amines and no bound species appear to be formed at room temperature.

Recently, Merkel *et al.*¹⁴ proposed a relationship between the $O_2(^1\Delta_g)$ quenching efficiency of organic solvents and the absorption spectrum of the solvent at 1270 nm and 1590 nm. Such a correlation does not seem to apply for the amines studied in the present work since, for example, triethylamine which is a much better quencher than diethylamine shows a much weaker absorption in both these regions.

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