115° (4 mm). The deuterium content could not be measured exactly.[23]

***cis*- (1a-*1*,7-d_3) and *trans*-2-(Aminomethyl-d_2)cyclohexanol-*2-d* (1b-*1*,7-d_3).** A mixture of **1a**-*1*,7-d_3 and **1b**-*1*,7-d_3 (6:4) was prepared in 58% yield by reduction of **9** with lithium aluminum deuteride: bp 110–115° (4 mm). Mass spectral analysis of the ketals **19** and **20** prepared from the diols **2** and **13** obtained from the deamination of this material showed that **1**-*1*,7-d_3 contained 6–7% dideuterated material.

***N*-Benzoyl derivative of 1b (10b)** was prepared as previously described[7c] in 90% yield: mp 120–122.5° (petroleum ether–benzene) (lit.[7a] mp 123–124°).

***cis*-2-(Aminomethyl)cyclohexanol (1a).** The inversion at C-1 was accomplished by treating **10b** with thionyl chloride.[7b] The acidic hydrolysis of the intermediate, **11**, gave **1a** in 40% yield: bp 105–108° (5 mm); nmr τ 5.97 (1 H, m, CHO), 7.18 (2 H, m, CH_2N), 8.0–9.0 (9 H, broad m, CH_2, CH), 7.31 (3 H, s, OH and NH_2). No **1b** was detected in the product by glc (<5%). The forerun consisted mainly of 1-(aminomethyl)cyclohexene (**23**).

Deamination Procedure. A solution of 31.5 mmol of sodium nitrite in 15 ml of water was added at once to an ice-cold solution of 30 mmol of amino alcohol (**1**) and 30 mmol of phosphoric acid in 30 ml of water. The resulting solution was stirred for 1.5 hr at 0° and 93–95 hr at room temperature. For product analysis, the solution was saturated with sodium chloride and thoroughly extracted with ether. The dried ($MgSO_4$) extract was concentrated and analyzed by glc (Table II). For identification, the components were isolated by preparative glc and subjected to ir and nmr analysis. Mass spectra were run directly from the mixture by glc–mass spectrometry.

In experiments with deuterated compounds, 25 ml of pentane was added immediately after the nitrite solution. At the end of the reaction, the water was frozen in a Dry Ice–acetone bath, and the pentane solution was separated. The aqueous solution was extracted two times with pentane by thawing–stirring–freezing cycles. The products **13a,b** and **2a,b** were isolated from the aqueous solution, as above. Products **4** and **14** were isolated from the pentane solution by concentration followed by either distillation in a short-path assembly at 100 mm or preparative glc. Mass spectra were determined by glc–mass spectrometry. In order to avoid errors due to isotopic fractionation during the chromatographic process, several mass spectra were run during the elution of each peak. No significant isotope fractionation was observed for any of the compounds investigated.

Attempts to isolate cyclohexanecarboxylic acid (**15**) from the deamination of **1a** by extraction with alkali led to a few milligrams of an unidentified oil. Similarly, dilution of the reaction product with alcohol did not precipitate any cyclohexanecarboxaldehyde trimer **16** (see below).

Reaction of Cyclohexanecarboxaldehyde (3) with Nitrous Acid. The same procedure as that used for amino alcohol **1** was followed. A partly solid, crude product was obtained which on dilution with ethanol gave 36% solid **16**: mp 199–200° (acetone) (lit.[43] mp 202–203°); nmr τ 5.49 (3 H, d, J = 4.5 Hz, CHO_2), 8.10–9.10 (33 H, broad envelope, CH_2, CH). Extraction of the mixture with base gave 35% cyclohexanecarboxylic acid (**15**). The remainder of the product consisted mainly of unreacted **3** (6%).

Reaction of 2-Methylenecyclohexanol (14) with Nitrous Acid. This reaction was performed with the mixture obtained from the lithium aluminum hydride reduction of ethyl 2-cyclohexanonecarboxylate. The same procedure as that used for amino alcohol **1** was followed except that K_2HPO_4 was used to buffer the reaction mixture at pH 5–6. The usual work-up procedure was used. The pentane extract contained mainly unreacted **14** and 1-(hydroxymethyl)cyclohexene (together 77% of the starting weight). No more than traces of 1-methylcyclohexanone (**4**) were found. The ether extract contained **2a**, **2b**, some 1-(hydroxymethyl)cyclohexene, and other minor compounds (all together 14% of the starting weight).

Reaction of 1-Methylcyclohexene Oxide (21) with Nitrous Acid. The same procedure as that used for 2-methylenecyclohexanol (**14**) was followed to yield **13a** (3%), **13b** (68%), and **4** (3%). Minor amounts of **14** and other unidentified products were also present.[25]

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[43] O. Wallach and E. Isaac, *Justus Liebigs Ann. Chem.*, 347, 328 (1906).

Kinetic Evidence for Both Quenching and Reaction of Singlet Oxygen with Triethylamine in Pyridine Solution

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Received April 2, 1971

Abstract: Kinetic evidence is presented which shows that, in pyridine solution, triethylamine is approximately 16 times as reactive an acceptor of singlet oxygen as 2-methyl-2-pentene, that it is as good a quencher of singlet oxygen as 1,4-diazabicyclo[2.2.2]octane, and that approximately nine quenching acts occur for every molecule of triethylamine which is destroyed by singlet oxygen.

Although it is well established that aliphatic amines may *quench* singlet oxygen,[1,2] it is not so well established that aliphatic amines may also *react* with singlet oxygen. Ogryzlo and Tang[2] found that, in the gas phase, reaction of singlet oxygen with aliphatic amines must be at least 100 times less efficient than quenching of the amines by singlet oxygen. Ouannes and Wilson[1] reported that the tertiary amines 1,4-diazabicyclo[2.2.2]octane (DABCO), ethyldiisopropylamine, *N,N,N′,N′*-tetramethylethylenediamine, and *N*-allylpiperidine were "apparently unreactive toward $^1O_2$" in bromobenzene solution, yet retarded the oxidation of 1,3-diphenylisobenzofuran, a known singlet oxygen acceptor.

There have been several reports of dye-sensitized oxygenations of amines. The earliest was that of Gaffron,[3] who found that erythrosin photosensitized the oxygenation of *n*-propylamine, and that chlorophyll photosensitized the oxygenation of isoamylamine. More recently Schenck[4] reported that dye-sensitized photooxygenation of primary, secondary, and tertiary amines results in the uptake of one, two, or three molecules of O_2, respectively, indicating that the number of α-CH groups determines the stoichi-

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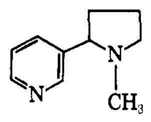
[1] C. Ouannes and T. Wilson, *J. Amer. Chem. Soc.*, 90, 6527 (1968).
[2] E. A. Ogryzlo and C. W. Tang, *ibid.*, 92, 5034 (1970).
[3] H. Gaffron, *Ber., Deut. Chem. Ges. B*, 60, 2229 (1927).
[4] G. O. Schenck, *Angew. Chem.*, 69, 579 (1957).

ometry. The products of these reactions were α-amine hydroperoxides. Others have reported a variety of reactions to occur when amines are irradiated in the presence of photosensitizing dyes and oxygen: α-oxidation,[5,6] β-oxidation,[7] dehydrogenation,[6,7] and dealkylation.[7]

These reactions may take place by either or both of two well-recognized mechanisms.[8] In type I photosensitized oxygenations (also known as the D-R mechanism[9]), the excited sensitizer interacts with the substrate to give a substrate radical. This radical may react with oxygen to give a substrate peroxy radical or undergo other reactions. Singlet oxygen is not involved in type I photooxygenations. In type II photooxygenations (also known as the D-O mechanism[10]), the substrate interacts with oxygen to give what is now generally accepted to be singlet oxygen. This in turn may react with the substrate. The balance between these two mechanisms will be determined by (1) the relative reactivity of the sensitizer triplet toward the substrate and O_2, and (2) the relative concentration of the substrate and oxygen.

One case in which it has been clearly demonstrated that singlet oxygen can react with an aliphatic amine is that of nicotine[11] (**1**). In methanol this amine consumes 3 mol of oxygen when irradiated in the presence of Rose Bengal and oxygen. Careful kinetic analysis showed that singlet oxygen is quenched by nicotine at a rate that is 5.4 times the rate at which it reacts with the amine. These data may be compared with some of Foote, *et al.*,[12,13] who measured the reactivity of DABCO as a singlet oxygen quencher in methanol as solvent,[12] and the reactivity of 2-methyl-2-pentene as a singlet oxygen acceptor in benzene–methanol (4:1, v:v) as solvent.[13] Assuming equal lifetimes of singlet oxygen in the two solvents, then nicotine is about one-third as reactive an *acceptor* of singlet oxygen as 2-methyl-2-pentene and about one-seventh as reactive a *quencher* as DABCO.



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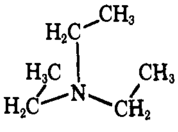
We have found, using kinetic techniques, that the dye-sensitized photooxygenation of triethylamine in pyridine is definitely a singlet oxygen reaction, *i.e.*, it is a type II, rather than type I, photooxygenation. Further, we also find that this amine (**2**) is as good a quencher of singlet oxygen as is DABCO (**3**). The rigid structure of DABCO apparently has little to do with its ability to quench.



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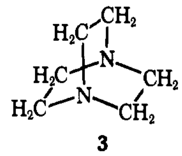

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Flexibility around the nitrogen atom, however, does favor reaction with singlet oxygen. We detect no reaction of **3** with singlet oxygen under conditions where photooxygenation of **2** is readily measured.

Results and Discussion

Irradiation through Pyrex glass of a pyridine solution containing 10^{-4} *M* Rose Bengal and 5.92×10^{-3} *M* triethylamine resulted in the uptake of 1.81×10^{-2} mol/l. of oxygen. This corresponds to a stoichiometry of 3.06 mol of oxygen per mol of amine, in agreement with the results of Schenck.[4]

The following scheme will serve for discussion.

Scheme I

$$\text{Sens }(S_0) \xrightarrow{h\nu} \text{Sens }(S_1) \longrightarrow \text{Sens }(T_1)$$

$$\text{Sens }(T_1) + O_2 \longrightarrow \text{Sens }(S_0) + {}^1O_2$$

$${}^1O_2 \xrightarrow{k_d} O_2$$

$${}^1O_2 + Q \xrightarrow{k_q} O_2 + Q$$

$${}^1O_2 + Q \xrightarrow{k_R} QO_2$$

This describes a type II photooxygenation in which the acceptor Q is capable not only of reaction with singlet oxygen, but also of quenching singlet oxygen. It is assumed that Q quenches neither sensitizer singlets nor triplets under the conditions of the experiment. The rate of oxygen absorption will be

$$\text{rate} = I_0abc\frac{k_R(Q)}{k_d + k_R(Q) + k_q(Q)} \tag{1}$$

where I_0 is the incident light intensity, *a* is the fraction of light absorbed by the sensitizer, *b* is the fraction of sensitizer singlets which undergo intersystem crossing, and *c* is the fraction of sensitizer triplets which transfer energy to oxygen to give singlet oxygen. The product I_0abc will be a constant (*C*) under the following conditions: (1) constant light intensity; (2) constant fraction of light absorbed by the sensitizer; (3) constant partial pressure of oxygen; and (4) no quenching of sensitizer singlets or triplets by Q. When Rose Bengal is used as a sensitizer for the photooxygenation of triethylamine, conditions 1–3 are easily satisfied. We shall prove later that condition 4 is also satisfied.

Inversion of eq 1 gives eq 2, where $C = I_0abc$ and

$$\text{rate}^{-1} = C^{-1}\left[1 + \frac{k_q}{k_R} + \frac{k_d}{k_R}\frac{1}{(Q)}\right] \tag{2}$$

is assumed constant as (Q) is varied. Figure 1 shows a plot according to this equation when Q = triethylamine, and Figure 2 (bottom line, squares) shows a similar plot when Q = 2-methyl-2-pentene. In the latter case, $k_q = 0$ (*i.e.*, the olefin reacts with, but does not quench, singlet oxygen), and so the intercept in this case is C^{-1}. This value may be applied to the line in Figure 1, from which we calculate k_d/k_R (= "β")

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[5] M. H. Fisch, J. C. Gramain, and J. A. Oleson, *Chem. Commun.*, 13 (1970).

[6] R. F. Bartholomew and R. S. Davidson, *ibid.*, 1174 (1970).

[7] F. C. Schaefer and W. D. Zimmerman, *J. Org. Chem.*, **35**, 2165 (1970).

[8] G. O. Schenck, *Ind. Eng. Chem.*, **55**, No. 6, 40 (1963).

[9] Y. Usui and M. Koizumi, *Bull. Chem. Soc. Jap.*, **40**, 440 (1967).

[10] Y. Usui, C. Iwanaga, and M. Koizumi, *ibid.*, **42**, 1231 (1969).

[11] G. O. Schenck and K. Gollnick, *J. Chim. Phys.*, **55**, 892 (1958).

[12] C. S. Foote, R. W. Denny, L. Weaver, Y. Chang, and J. Peters, *Ann. N. Y. Acad. Sci.*, **171**, 139 (1970).

[13] C. S. Foote and R. W. Denny, *J. Amer. Chem. Soc.*, **90**, 6233 (1968).

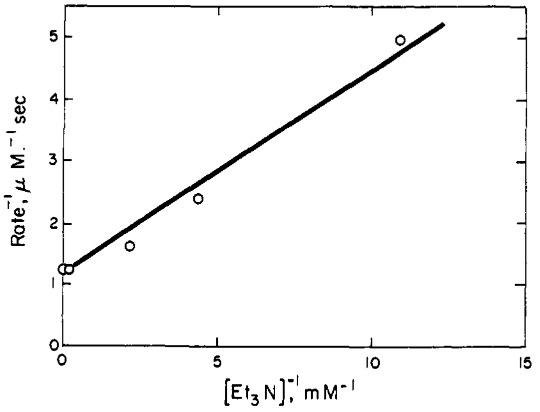

Figure 1. Photooxygenation of triethylamine. Dependence of rate on amine concentration; 546-nm light filtration.

= 0.0027 M, and $k_q\tau = 3.5 \times 10^3\ M^{-1}$ (where $\tau = 1/k_d$) for triethylamine in pyridine.

In order to compare the reactivity (β) and quenching constant ($k_q\tau$) for triethylamine with a known singlet oxygen acceptor (2-methyl-2-pentene) and quencher (DABCO), we use Scheme II. In this scheme, A = olefin and Q = a quencher (*e.g.*, DABCO), which does *not* react with singlet oxygen. This is similar to the scheme given by Foote and Denny[13] for quenching of the dye-sensitized photooxygenation of 2-methyl-2-pentene by β-carotene. The rate of oxygen absorption will be given by

Scheme II

$$\text{Sens (S}_0) \xrightarrow{h\nu} \text{Sens (S}_1) \longrightarrow \text{Sens (T}_1)$$

$$\text{Sens (T}_1) + \text{O}_2 \longrightarrow \text{Sens (S}_0) + {}^1\text{O}_2$$

$${}^1\text{O}_2 \xrightarrow{k_d} \text{O}_2$$

$${}^1\text{O}_2 + \text{A} \xrightarrow{k_A} \text{AO}_2$$

$${}^1\text{O}_2 + \text{Q} \xrightarrow{k_q} \text{O}_2 + \text{Q}$$

$$\text{rate} = C\frac{k_A(\text{A})}{k_d + k_q(\text{Q}) + k_A(\text{A})} \qquad (3)$$

and the inverse rate by

$$\text{rate}^{-1} = C^{-1}\left[1 + \frac{k_d + k_q(\text{Q})}{k_A}\,\frac{1}{(\text{A})}\right] \qquad (4)$$

Here C has the same meaning as before. To use eq 4 requires that A neither react with nor quench sensitizer singlets or triplets. Since (A) is varied while (Q) is held constant, the ratio of slope/intercept will not depend upon whether Q quenches or reacts with sensitizer.

Two plots are given in Figure 2 using this equation. The first is the bottom line in Figure 2 (squares), which is the special case in which quencher is absent ((Q) = 0). This was discussed previously in connection with eq 2. In this case, k_A(A) of eq 4 is the same as $k_R \cdot$ (Q) of eq 2, and the two equations are identical. From this line, we find k_d/k_A (= β) = 0.043 M for 2-methyl-2-pentene in pyridine. Foote and Denny[13] obtained a similar β value, 0.04 M, for 2-methyl-2-pentene in 1:1:1 methanol–benzene–diglyme.

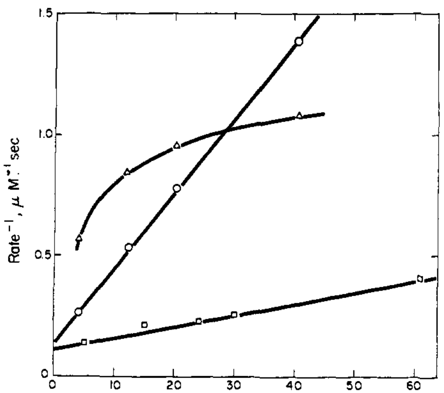

Figure 2. Dependence of rate of oxygen absorption on olefin concentration in the presence of: △, 1.05 × 10^{-2} M triethylamine; ○, 0.90 × 10^{-3} M DABCO; □, no added amine; 546-nm light filtration.

In the presence of 0.90 × 10^{-3} M DABCO, the second straight line in Figure 2 (circles) was obtained. From the slope/intercept we calculate, using eq 4, that $k_q\tau = 4.3 \times 10^3\ M^{-1}$ for DABCO in pyridine. This may be compared to the value 1.6 × 10^2 M^{-1} obtained by Foote, *et al.*,[12] in methanol as solvent.

These data, taken with the previously discussed triethylamine data, lead to the following conclusions. (1) Triethylamine is approximately 16 times as reactive an *acceptor* of singlet oxygen as 2-methyl-2-pentene (k_d/k_A = 16). (2) It is as good a *quencher* of singlet oxygen as DABCO. (3) Approximately 9 quenching acts occur for every molecule of triethylamine which is destroyed by singlet oxygen (k_q/k_R = 9.4).

As mentioned above, the use of eq 2 to determine the reactivity and quenching constants for triethylamine requires that the amine does not quench sensitizer singlets or triplets under the conditions of the experiment. We can discount this possibility for the following reasons. (1) If Q (eq 2) quenched sensitizer singlets or triplets, C would vary with (Q) and a plot of rate^{-1} *vs.* (Q)$^{-1}$ would exhibit curvature. (2) Although high concentrations of DABCO will quench the fluorescence of Rose Bengal ($k_q\tau$ = 6.7 M^{-1}), no detectable fluorescence quenching was observed with triethylamine concentrations as high as 0.66 M. (3) Photooxygenation of a 0.2 M triethylamine solution took place with a rate (oxygen absorption) of 0.79 μM sec^{-1} in air-saturated pyridine, and 0.72 μM sec^{-1} in oxygen-saturated pyridine. The absence of an oxygen pressure dependency makes it very unlikely that triethylamine is competing with oxygen for Rose Bengal triplets. (4) When a degassed pyridine solution of Rose Bengal was flashed in the presence of 10^{-2} M triethylamine, the decay curve was superimposable on that obtained in the absence of amine.[14]

We have tested our results in two ways. First, we used triethylamine as a quencher for the photooxygenation of 2-methyl-2-pentene. The curve in Figure 2 (triangles) shows data for this reaction when plotted according to eq 4. Whereas DABCO gives a straight line for such an experiment (Figure 2, circles), with triethylamine, rates become too high at low olefin concentrations. This is because photooxygenation of

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[14] We are indebted to Dr. W. G. Herkstroeter for this experiment.

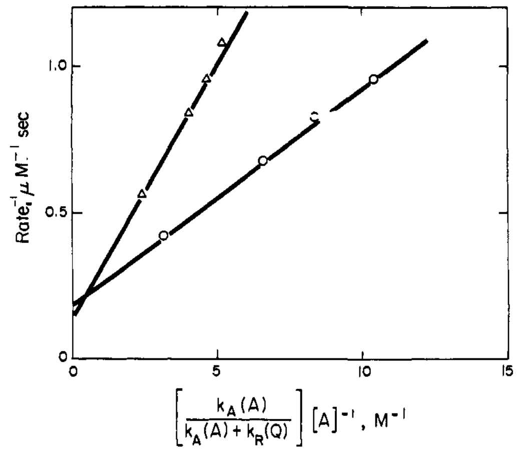


Figure 3. Dependence of rate of oxygen absorption on corrected olefin concentration: △, 1.05×10^{-2} *M* triethylamine; ○, 4.45×10^{-3} *M* triethylamine; 546-nm light filtration.

triethylamine becomes increasingly important as the olefin concentration decreases.

What must be done is to combine Schemes I and II, and derive an equation for the rate of photooxygenation when the quencher is able to react with singlet oxygen. Equation 5 was derived on this basis. This

$$\text{rate}^{-1} = C^{-1}\left\{1 + \frac{k_d + k_q(Q)}{k_A}\left[\frac{k_A(A)}{k_A(A) + k_R(Q)}\frac{1}{(A)}\right]\right\} \tag{5}$$

equation collapses to eq 4 when $k_R = 0$. When the data in Figure 2 (triangles) are replotted according to eq 5, the top line in Figure 3 is obtained (triangles). The other line in this figure is for a similar experiment at a lower amine concentration. The abscissa in Figure 3 may be viewed as a corrected (inverse) olefin concentration, *i.e.*, the concentration of olefin that would be necessary to obtain the observed rate if triethylamine quenched, but did not react with, singlet oxygen. From the data in Figure 3, we calculate $k_q\tau = 2.4 \times 10^3 \pm 0.2 \times 10^3$ M^{-1} for triethylamine, in reasonable agreement with the data calculated from Figure 1. Furthermore, the fact that the intercepts are the same at both concentrations of amine and are equal (within experimental error) to the intercepts in Figure 2 supports the previous conclusion that triethylamine (as well as DABCO) is neither reacting with nor quenching Rose Bengal singlets or triplets under the conditions of these experiments.

A second test of the above results was made by studying the photooxygenation of triethylamine when quenched by DABCO. For this system we use Scheme III, in which Q = triethylamine and Q′ = DABCO.

Scheme III

$$\text{Sens }(S_0) \xrightarrow{h\nu} \text{Sens }(S_1) \longrightarrow \text{Sens }(T_1)$$

$$\text{Sens }(T_1) + O_2 \longrightarrow \text{Sens }(S_0) + {}^1O_2$$

$${}^1O_2 \xrightarrow{k_d} O_2$$

$${}^1O_2 + Q \xrightarrow{k_R} QO_2$$

$${}^1O_2 + Q \xrightarrow{k_q} O_2 + Q$$

$${}^1O_2 + Q' \xrightarrow{k_q'} O_2 + Q'$$

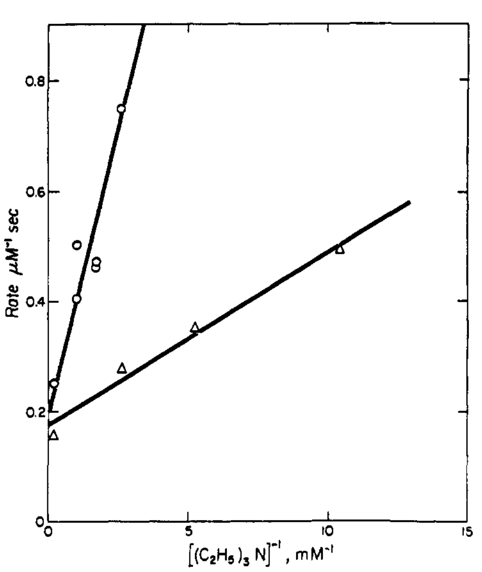


Figure 4. Photooxygenation of triethylamine: △, no added quencher; ○, 1.41×10^{-3} *M* DABCO added; Pyrex light filtration.

The rate of oxygen absorption will be

$$\text{rate} = C\left[\frac{k_R(Q)}{k_d + k_R(Q) + k_q(Q) + k_q'(Q')}\right] \tag{6}$$

By plotting the inverse rate *vs.* the inverse triethylamine concentration (eq 7), while holding the DABCO concentration

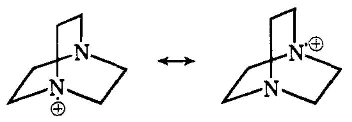
$$\text{rate}^{-1} = C^{-1}\left[1 + \frac{k_q}{k_R} + \frac{k_d + k_q'(Q')}{k_R}\frac{1}{(Q)}\right] \tag{7}$$

constant, one should obtain a straight line with a slope intercept (S/I) of $k_d + k_q'(Q')/(k_q + k_R)$. This experiment may be repeated in the absence of DABCO, where now $S_0/I_0 = k_d/(k_q + k_R)$. Dividing S/I by S'/I' gives

$$\frac{S/I}{S'/I'} = 1 + k_q'\tau\,(Q') \tag{8}$$

where $k_q'\tau$ is the quenching constant for DABCO. The data are shown in Figure 4. It is clear that DABCO quenches the photooxygenation of triethylamine. From the data we calculate $k_q'\tau = 3.1 \times 10^3$ M^{-1} for DABCO, in reasonable agreement with the value (4.3×10^3 M^{-1}) calculated from the quenching of the photooxygenation of 2-methyl-2-pentene.

The fact that triethylamine and DABCO have essentially equal quenching constants in pyridine shows that transannular stabilization of the DABCO radical cation[15] contributes little to its quenching ability. Even in the gas phase[2] these two amines have



similar quenching constants, and thus pyridine does not exert a leveling effect.

The principal difference between our results in pyridine solution and Ogryzlo and Tang's in the gas phase is that the polar solvent enhances the reactivity of tri-

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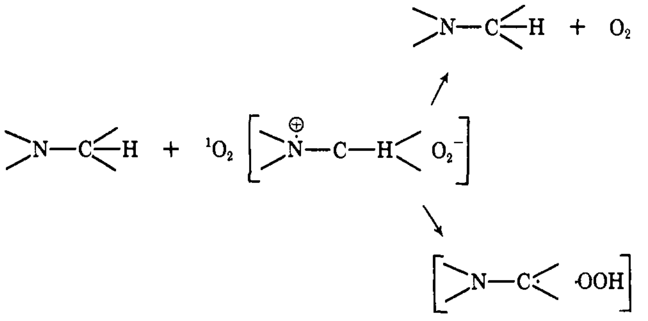
[15] T. M. McKinney and D. H. Geske, *J. Amer. Chem. Soc.*, 87, 3013 (1965).

ethylamine toward singlet oxygen by a minimum of one order of magnitude. Ogryzlo and Tang were unable to detect any reaction of triethylamine with singlet oxygen even after more than 100 deactivating collisions per amine molecule. In contrast, in pyridine solution one amine molecule is destroyed per nine deactivating collisions. This difference may result from the longer lifetime of the amine radical cation in solution, allowing proton transfer to O_2^- to occur in competition with back transfer of an electron from O_2^- to the amine radical cation.



The fact that proton transfer does not occur from $DABCO^{\cdot +}$ suggests that the amine radical must gain some stabilization from resonance structures of the type $>\cdot N{=}C<$. Such contributions to a resonance hybrid cannot occur with the rigid, bicyclic amine.

Experimental Section

A. Materials. Pyridine was Eastman grade, used without further purification. Rose Bengal (Eastman grade, C.I. 45440, 84% dye content) was purified by dissolving 2 g in the minimum amount of 0.14 *M* NH_4OH, and passing this over a 2 × 20 in. bed of Sephadex G-25 Fine (Pharmacia Fine Chemicals, Inc.) using water as eluent. Several bands were obtained, the main one being collected and acidified with dilute HCl, and the Rose Bengal free acid collected by filtration. After drying, a 1.14×10^{-4} *M* solution in pyridine had a λ_{max} at 573 nm with D_{573} 1.13, D_{546} 0.35, both for 1-mm layers. The dye does not follow Beer's law, the D_{max} shifting hypso- and hyperchromically upon dilution. 2-Methyl-2-pentene was Phillips Petroleum Company pure grade, 99 mol % minimum. This was passed over a short column of aluminum oxide (Woelm Neutral) prior to use. Triethylamine was Eastman grade, once distilled.

B. Measurements. The reactions were followed by measuring the rate of oxygen consumption in a constant pressure, automatic recording gasometer apparatus. This apparatus is basically a hybrid of two that are described in the literature.[16,17] The absorption cell was similar to the one described by Mahoney, *et al.*,[16] and the physical arrangement of the gasometer itself was similar to that of Traylor and Russell.[17] Pressure differentials were detected by a Schaevitz P476-A10 pressure transducer (0–10 in. of water), which was attached to the gasometer *via* small-diameter, stainless steel tubing with Swagelok fittings (Teflon front ferrules). The signal from the transducer activated a Harvard infusion–withdrawal pump. This pumped mercury into a gas buret attached to the gasometer until the null point of the transducer was reached. The pump displacement was converted to a voltage change by appropriate gearing of the pump to a Helipot linear potentiometer. Output from the potentiometer was fed into a 10-mV span strip chart recorder, equipped with chart speeds of 2, 5, 8, and 20 in./hr (Varian Associates Model G11A). Rates as low as 10^{-7} *M* sec^{-1} can be measured on a 10-ml sample.

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[16] L. R. Mahoney, R. W. Bayma, A. Warnick, and C. H. Ruoff, *Anal. Chem.*, **36**, 2516 (1964).

[17] T. G. Traylor and C. O. Russell, *J. Amer. Chem. Soc.*, **87**, 3698 (1965).

Kinetics of the Formation of Imines from Isobutyraldehyde and Primary Aliphatic Amines with Polar Substituents[1]

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Abstract: The kinetics of the reaction of isobutyraldehyde with *n*-propylamine, 3-methoxypropylamine, 2-methoxyethylamine, 2,2-dimethoxyethylamine, and 2,2,2-trifluoroethylamine to give the corresponding imines have been studied by stopped-flow spectrophotometry in aqueous solution at pH's around the pK_a of the conjugate acids of the amines and higher at 35°. The formation of the intermediate carbinolamines was too fast to follow; the equilibrium constant K_{ca} for carbinolamine formation was found to be decreased somewhat by electron-withdrawing and bulky substituents. The overall second-order rate constants for imine formation were found to be independent of the pH above about pH 10 and proportional to the hydrogen-ion concentration below about pH 9 in the cases where rate measurements could be made at this low a pH. The second-order rate constants for the uncatalyzed reaction were greatly decreased by electron-withdrawing substituents but were relatively insensitive to the differences in steric effects among the amines studied.

Previous studies have shown that the α-hydrogen exchange reactions of aldehydes and ketones may be catalyzed by a mixture of a primary amine salt and a base.[2–5] The primary amine salt transforms the carbonyl compound partially to an equilibrium mixture of an imine and an iminium ion, whose α-hydrogen atoms are much more acidic than those of the carbonyl

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