

CARBON DIOXIDE AS A QUENCHER OF FLUORESCENCE

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Abstract

Carbon dioxide is found to form a reversible quench complex with the excited singlet states of certain amines. No separate exciplex emission could be observed and the complexation was not dependent on solvent polarity. Irradiation leads to photochemical products.

Carbon dioxide is not known to form complexes with electronically excited molecules and has often been used as a thermalizing gas in vapour phase fluorescence. There would be even less reason for believing that carbon dioxide would have any effect on electronically excited states in solution.

Sasse¹ recently found that saturation with carbon dioxide could lower the quantum yield of photoadduct of naphthalene known to be formed through a singlet excited state.

Because of this anomalous effect and its obvious implications for photosynthetic systems, the effect of carbon dioxide on the fluorescence of a number of aromatic compounds in solution was investigated.

The saturation with carbon dioxide of previously deoxygenated solutions of many compounds has been found to have no effect on the shape or intensity of their fluorescence. Compounds which are unaffected include benzene and derivatives (cyano-, 1,4-dicyano-, methoxy-, 1,3-dimethoxy-, and phenol), naphthalene and derivatives (1-cyano-, 2-methoxy-), perylene, indole, popop, rhodamine-B and a number of amines (aniline, diphenylamine, triphenylamine, *N,N*-dimethylnaphthylamine). The fluorescence of some typical exciplexes was similarly unaffected.

There were three compounds for which there was a definite quenching effect: *dimethylaniline*, *diethylaniline* (and presumably higher homologues), and *1,4-diazabicyclo[2,2,2]octane* known as dabco.

For each of these compounds, the effect of saturation of the solution with carbon dioxide was to lower the fluorescence quantum yield but not to change the distribution of fluorescence intensity nor to produce a new (long-wavelength) emission which might have been attributable to an exciplex (even when the temperature was

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¹ Sasse, W., personal communication.

dropped to -50°C with concomitant increase in carbon dioxide solubility). Table 1 gives the saturation concentration of carbon dioxide in various solvents² recalculated for 298 K and 96 kJ m^{-3} (720 Torr—local pressure), and the rate constant for bimolecular collisions as calculated in the usual manner ($k_{\eta} = 8RT/2000\eta$ where η is the viscosity of the solvent). This is then compared to the experimental bimolecular rate constant for quenching k_q . The experimental quenching rate constant is much smaller

TABLE 1
QUENCHING OF DIETHYLANILINE BY CARBON DIOXIDE IN VARIOUS SOLVENTS
(298 K; pressure 96 kJ m^{-3})

	Cyclohexane	Benzene	Methanol	Methyl acetate
$\text{CO}_2/(\text{mol l}^{-1})$	0.066	0.091	0.148	0.249
$10^{-9}k_{\eta}/(\text{l. mol}^{-1}\text{ s}^{-1})$	11.3	15.4	16.3	26.3
$10^{-9}k_a/(\text{l. mol}^{-1}\text{ s}^{-1})$	0.57	1.07	0.75	0.46

than and uncorrelated with the rate constant calculated from diffusion. Generally quenching by gases such as oxygen gives larger quenching rate constants than calculated. This suggests the formation of a weak dissociative quench complex which is responsible for the loss of only a small proportion of energy from the system. This is confirmed by the temperature dependence of the quenching reaction which requires the existence of a dissociative rate constant. With increasing temperature the viscosity of the solvent and the saturation concentration of carbon dioxide both decrease and these factors oppose one another in their influence on the rate of quenching (Table 2). If the rate constant for bimolecular collisions based on diffusion is given by

$$k_{\eta} = 8RT/2000\eta$$

then the Stern–Volmer quenching equation reads

$$(\phi_0/\phi_1 - 1)\eta/(T[\text{CO}_2]) = 8R/\{2000(1 + k_a\tau)\} \quad (1)$$

where k_a is the rate of dissociation of the quench complex and τ is its intrinsic lifetime.

TABLE 2
TEMPERATURE DEPENDENCE OF THE QUENCHING OF THE FLUORESCENCE OF
DIETHYLANILINE (IN TOLUENE) BY CARBON DIOXIDE

	0°C	30°C	43°C
Ratio of unquenched to quenched fluorescence	1.36	1.22	1.18
$10^3 \times \text{solvent dynamic viscosity}^a/(\text{J m}^{-3}\text{ s})$	0.772	0.526	0.45
Concentration of $\text{CO}_2/(\text{mol l}^{-1})$	0.136	0.088	0.075
$(\phi_0/\phi_1 - 1)\eta/(T[\text{CO}_2])$	0.0074	0.0043	0.0034

^a From "Handbook of Chemistry and Physics" (Chemical Rubber Publishing Co.: Cleveland, Ohio).

Increasing temperature can only decrease τ so that the experimentally observed result that the left-hand side of equation (1) decreases with increasing temperature (at a rate greater than $1/T$) is indicative of an increase in k_a . These results lead to a minimum

² Seidell, A., "Solubilities of Inorganic and Metal-Organic Compounds" (American Chemical Society: Washington 1958).

value for the enthalpy of formation of carbon dioxide quench complex of -1.7 kJ mol^{-1} which is about one order of magnitude smaller than that of more typical excimers and exciplexes. The results for dimethylaniline are very similar, while dabco is quenched very much more strongly, doubtless as a result of its much longer lifetime (c. 100 ns in solution).

The quenching is not correlated with solvent polarity so that there do not appear to be lower-lying solvated ion states. Carbon dioxide has an electron affinity of 3.8 eV,³ several electron volts higher than those of the aromatic hydrocarbons which commonly act as electron acceptors for dialkylaniline exciplexes. These results led Sasse to search for and find unstable photochemical products from tertiary amines and carbon dioxide¹ so that there appears to be predictive value in the quenching experiments. The wider significance for redox processes occurring in photosynthesis is yet to be explored.

³ Buckel'nikova, N. S., *Usp. fiz. Nauk*, 1958, **65**, 351.