Chemiluminescent Recombination of Formyl Radicals

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DURING studies of certain hydrogen-atom reactions a greenish luminescence has been observed when formaldehyde is added to the products of a microwave discharge through molecular hydrogen (2%) flowing on an inert-gas carrier, at pressures of about 1 mm.Hg. The emission has been photographed in first and second orders of a Bass–Kessler spectrograph. The banded spectrum up to about 5600 Å (apparently diffuse at this resolution) has been identified as belonging to the ^1A_u–^1A_g system of glyoxal,[1] on the basis of multiple coincidences of band positions with those recorded in fluorescence by Thompson.[2] It is seen here for the first time in chemiluminescence. That the emitter is glyoxal is confirmed by the observed dependence of the intensity of emission on the square of the formaldehyde concentration, clearly the result of reaction, second order in formyl radicals. Recombination of formyl radicals has been suggested elsewhere[3] to explain the presence of glyoxal in a similar system.

The low wavelength limit of the spectrum occurs at 3965 Å and clearly the corresponding energy of 25220 cm.$^{-1}$ should be an upper limit to the energy of the bond formed. Assuming zero activation energy for recombination of formyl radicals, and using an average kinetic energy of 100 cm.$^{-1}$ $(=\frac{1}{2}kT)$ for each, the dissociation energy D_0 of the carbon–carbon bond in glyoxal is $71\cdot5 \pm 0\cdot3$ kcal./mole, where the error limit represents the uncertainty in determining the wavelength cut-off. (The temperature coefficient of the observed intensity of emission appears to be about $+2$ kcal./mole. However, until it is established whether this is associated with the actual recombination reaction rather than with other reactions controlling the concentration of formyl, it is not allowed for in the calculated dissociation energy.) Utilising a latent heat of fusion of glyoxal of $2\cdot0 \pm 1\cdot0$ kcal./mole (arrived at from established data on comparable molecules) together with its known heat of vapourisation and measured heat of formation of the solid,[4] ΔH_f° for the gas at 1 atm. is estimated to be $-72\cdot7$ kcal./mole. From this the following additional quantities may be derived: ΔH_f° (CHO) $= -0\cdot6$ kcal./mole, $D(\mathrm{H-CO}) = 26\cdot3$ kcal./mole, $D(\mathrm{H-CHO}) = 79\cdot2$ kcal./mole. This value of $D(\mathrm{H-CHO})$ is in agreement with the latest electron impact study[5] which gives $79\cdot5$ kcal./mole, and also with the observation that free radical breakdown of formaldehyde can be induced by light of 3650 Å ($78\cdot3$ kcal./mole).[6] The same value is compatible moreover with the requirement that the dissociation limit lie below the predissociation which sets in at $82\cdot3$ kcal./mole in the lowest excited singlet state ($^1A''$) of formaldehyde.[7] It remains difficult however to reconcile the kinetically derived $D(\mathrm{H-CHO})$ which are some 10 kcal./mole higher,[8] with the data from these several consistent sources. It should be pointed out here that an alternative value of ΔH_f° (glyoxal) $= -54\cdot1$ kcal./mole based on bond additivity, is in much better agreement with the kinetic $D(\mathrm{H-CHO})$. We hope therefore soon to be able to redetermine the thermochemical ΔH_f° of glyoxal.

Preliminary study of the decay of the emission shows the system to be more complex kinetically than would appear at first sight. The chemiluminescence is observed strongly at concentrations of H atoms which are some 2% of those normal in such a flow system. At these levels impurity atoms may be playing an important part. For these reasons no detailed description of the kinetics can yet be made. It does seem apparent however that some species X is abstracting H from formaldehyde, to produce CHO radicals in concentration maintained in a low steady state by incompletely specified removal reactions.
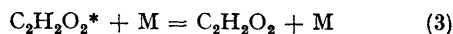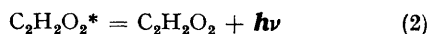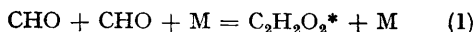
In addition to emission from the glyoxal molecule a more discretely banded system is observed, which overlaps the glyoxal system and extends with an intense band at 5703 Å into the near infrared. The intensity of the red system relative to the green decreases substantially with increasing concentration of formaldehyde. A second molecule, as yet unidentified but probably polyatomic, emitting with an intensity dependent on the formyl radical concentration to a power less than second order, is indicated.

The total emission is strongly quenched by traces of nitric oxide. Absence of significant quenching by NO, of glyoxal excited by a Tesla discharge through glyoxal[9] flowing on argon, confirms the effect of NO to be chemical in nature and the result of its reaction with a precursor of the excited glyoxal molecule. (The known[10] effect of NO in quenching triplet glyoxal cannot explain all the relevant observations.) If the reaction is with the formyl radical itself, the molecule HCONO recently observed in flash photolysis by Norrish[11] is a possible intermediate product, particularly in view of the complete absence of

quenching by molecular oxygen, which would be expected to behave similarly to NO in the alternative hydrogen abstraction reaction from CHO.

Nitric oxide much diluted with argon has been used to "titrate" the emission, and the critical NO concentration (6.5×10^{-12} moles/cc.) has been tentatively equated to CHO concentration. The corresponding light intensity I was measured and the two values substituted in the expression $I = I_0[CHO]^2$. Using the same geometry and photomultiplier-filter combination to observe the air-afterglow intensity $I_a = I_{0a}[O][NO]$ at known oxygen atom and nitric oxide concentrations, a value of I_{0a} in the same arbitrary units as I_0 was separately determined. Allowing a factor of 6 for the fact that the spectral distribution of the glyoxal system is confined to the blue and green regions whereas the air-afterglow extends well into the red,[12] it is concluded that the absolute emission intensity I_0 for glyoxal is some 50 times greater than that for the air-afterglow, i.e., is about 2×10^9 cc. mole^{-1}sec.$^{-1}$.

The following scheme will control the emission intensity (assuming termolecular recombination at these low pressures):

$$CHO + CHO + M = C_2H_2O_2^* + M \qquad (1)$$

$$C_2H_2O_2^* = C_2H_2O_2 + h\nu \qquad (2)$$

$$C_2H_2O_2^* + M = C_2H_2O_2 + M \qquad (3)$$

which gives $\quad I_0 = \dfrac{k_1 k_2(M)}{k_2 + k_3(M)}$

By use of the approximate f-value of 0.0004 quoted by McMurry[13] for the ^1A_u–^1A_g system, a k_2 of 1.3×10^4 sec.$^{-1}$ is derived. At pressures greater than 1 mm.Hg radiation will therefore be negligible in comparison with collisional quenching of excited glyoxal. Hence $k_1/k_3 = 1.5 \times 10^5$ cc.mole^{-1}. This is a very reasonable value consistent with k_3 lying between 10^{12} and 10^{13} cc.mole^{-1}sec.$^{-1}$ (cf., k_{3a} of the air-afterglow[14]), and k_1 between 1.5×10^{17} and 1.5×10^{18} cc.^{2}mole^{-2}sec.$^{-1}$ (cf., the termolecular recombination rate constants for small organic radicals such as CH_3O, CH_3, with NO).[15]

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