Energy Transfer in the Photolysis of Biacetyl

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VIBRATIONAL–VIBRATIONAL energy transfer has an important effect on the quantum yields of primary processes in the gas-phase photolysis of organic molecules,[1–3] but no systematic results have yet been reported. This is mainly due to the difficulties in isolating this effect from the other ways in which an "inert molecule" can modify the mechanism of the photolysis,[4] *viz.* by deactivating the excited triplet state,[5] or by favouring non-radiative intersystem crossing.[6]

Biacetyl, owing to the constant value of the phosphorescence yield at long wavelengths,[1] seems a system in which the second possibility can be disregarded. We have therefore developed a method for studying the relative efficiencies of third bodies in deactivating vibrationally excited singlets in the photolysis of biacetyl under conditions in which this effect can be isolated and the influence of quenching impurities is minimized.

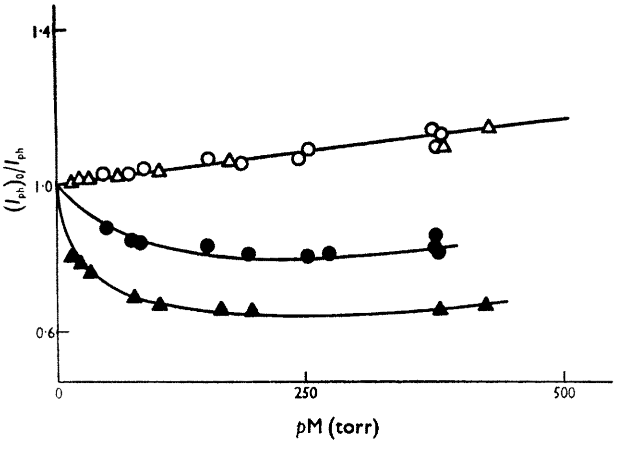

FIGURE 1. *Volmer plots for the photolysis of biacetyl in the presence of butane*: ○ *biacetyl* 18 *torr*, 4350 A; ● *biacetyl* 18 *torr*, 3660 A; △ *biacetyl* 8·9 *torr*, 4350 A; ▲ *biacetyl* 8·9 *torr*, 3660 A.

The photolysis of biacetyl in the presence of a third body, M, can be represented by equations (1)—(10)

$$\mathrm{B} + h\nu \rightarrow {}^1\mathrm{B}^* \qquad (1)$$

$${}^1\mathrm{B}^* \rightarrow \text{Products (or B} + h\nu) \qquad (2)$$

$${}^1\mathrm{B}^* + \mathrm{B} \rightarrow {}^1\mathrm{B} + \mathrm{B} \qquad (3)$$

$${}^1\mathrm{B}^* + \mathrm{M} \rightarrow {}^1\mathrm{B} + \mathrm{M} \qquad (4)$$

$${}^1\mathrm{B} \rightarrow {}^3\mathrm{B} \qquad (5)$$

$${}^1\mathrm{B} \rightarrow \mathrm{B} \qquad (6)$$

$${}^3\mathrm{B} \rightarrow \mathrm{B} + h\nu \qquad (7)$$

$${}^3\mathrm{B} + \mathrm{B} \rightarrow \mathrm{B} + \mathrm{B} \qquad (8)$$

$${}^3\mathrm{B} + \mathrm{M} \rightarrow \mathrm{B} + \mathrm{M} \qquad (9)$$

$${}^3\mathrm{B} \rightarrow \mathrm{B} \qquad (10)$$

where, if the hard sphere model is assumed,[3] k_2 will be the only rate constant sensitive to the incident wavelength. If this mechanism is accepted,

$$Y = \frac{(I_{\mathrm{ph}})_0}{I_{\mathrm{ph}}} = \frac{k_3p\mathrm{B}}{k_2 + k_3p\mathrm{B}} \times \frac{k_7 + k_8p\mathrm{M} + k_9p\mathrm{B} + k_{10}}{k_7 + k_9p\mathrm{B} + k_{10}} \times \frac{k_3p\mathrm{B} + k_4p\mathrm{M} + k_2}{k_3p\mathrm{B} + k_4p\mathrm{M}} \qquad (11)$$

where $(I_{\mathrm{ph}})_0$ is the phosphorescence when only biacetyl is present at a pressure $p\mathrm{B}$ and I_{ph} is the phosphorescence when a pressure $p\mathrm{M}$ of gas is added.

Equation (11) shows that a Volmer plot will give a straight line only when

$$k_2 \ll k_3p\mathrm{B} + k_4p\mathrm{M} \qquad (12)$$

this condition being most probably fulfilled at long wavelengths. For the 4350 Å radiation, a reasonable straight line can be drawn through the experimental points. At 3660 Å, the completely different shape of the Volmer plot indicates that this assumption does not hold, *i.e.* k_2 is competing with the vibrational deactivation.

When the data for the two incident wavelengths are related, a new function f can be derived:

$$f = \frac{Y_{3,660}}{Y_{4,360} - Y_{3,660}} = \frac{k_3p\mathrm{B}}{k_2} + \frac{k_3p\mathrm{B}}{k_4}\left(1 + \frac{k_3p\mathrm{B}}{k_2}\right)\frac{1}{p\mathrm{M}} \qquad (13)$$

where all the rate constants refer to the states reached with the 3660 Å incident light and the hard sphere collision hypothesis has been assumed.

A plot of f against $1/p\mathrm{M}$ is linear (Figure 2) and gives values of the relative rate constants k_3/k_2 and k_4/k_3. This second ratio shows the efficiency of the added gas relative to that of the parent molecule.

Values of k_3/k_2 and k_4/k_3 (Figure 2) are shown in the Table; values for cyclohexane derived from Ishikawa and Noyes data[1] are also included

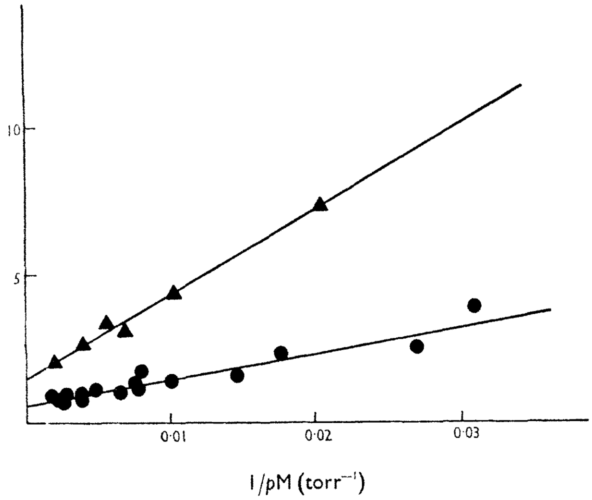

FIGURE 2. *Plot of* f *against* 1/pM: ▲ *biacetyl* 18 *torr*; ● *biacetyl* 9 *torr*; M = *carbon dioxide.*

The values of k_3/k_2 do not show any systematic dependence upon the biacetyl pressure, or the third body employed, and the values of k_4/k_3 (estimated error 10%) are independent of biacetyl pressure and wavelength. The relative efficiences of the third bodies employed strongly parallel those found in other systems.[7]

pM	pB(torr)	k_3/k_2(torr^{-1})	k_4/k_3
CO_2	18	0·077	0·17
CO_2	9	0·055	0·14
butane	18	0·066	0·59
butane	8·9	0·077	0·72
cyclohexane	0·16	0·069	0·68
cyclohexane	7·0	0·043	0·70
cyclohexane*	30	0	0·71

* For 3130 Å radiation

The method here employed is sensitive neither to small amounts of impurities in the third bodies employed nor to traces of oxygen, as their effect would cancel out in the function *f*.

The suggested reaction scheme is thus fully representative of the behaviour of the system and is suitable for quantitative studies on vibration–vibrational energy-transfer processes.

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