Energy Transfer and Cyclopentenone

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Summary The rate constant of $6{\cdot}1 \times 10^5\ \text{M}^{-1}\ \text{sec}^{-1}$ for quenching of benzophenone emission by cyclopentenone requires the triplet energy of cyclopentenone to be in the range of 73—74 kcal/mole.

IT was suggested[1] that cyclopentenone underwent photoannelation reactions from a higher triplet. Subsequent work made this appear unlikely,[2] and the problem has now been re-investigated. The reasons for the original conclusion were two-fold. First, the triplet energy of cyclopentenone as measured by equilibration methods, was found to be 60 kcal/mole[3] whilst it had clearly been shown that sensitisers of near 74 kcal/mole were necessary to initiate photo-annelation. Secondly, it was found that cyclopentenone quenched the photoreduction of benzophenone in isopropyl alcohol at an apparently close to diffusion-controlled rate.[4]

We have since shown[5] that enone energies, as measured by the photoequilibration method using stilbene, *i.e. the effective triplet energy* available for transfer, are, in cases where it can be determined,[6] about 10—15 kcal/mole below the 0–0 energy determined spectroscopically. Franck–Condon factors probably restrict the effective transfer of more energy from the enone.[5,6]

With the observation[7] of the phosphorescence of benzophenone at room temperature a direct test of the second premise was possible. We have now measured the quenching of benzophenone (8×10^{-2} M) phosphorescence in carbon tetrachloride solution with cyclopentenone (0·0—0·6 M). The exciting beam was at 380 nm and the relative intensity of the emission at 453 was monitored using a Jarrel–Ash monochrometer equipped with an EMI 6256 photomultiplier. With the terms defined in the following mechanism:

$$\text{B} \xrightarrow{I} {}^3\text{B}$$

$${}^3\text{B} \xrightarrow{k_\text{p}} \text{B} + h\nu$$

$${}^3\text{B} \xrightarrow{k_\text{t}} \text{B}$$

$$\text{K} + {}^3\text{B} \xrightarrow{k_2} {}^3\text{K} + \text{B}$$

$${}^3\text{K} + \text{B} \xrightarrow{k_{-2}} \text{K} + {}^3\text{B}$$

$${}^3\text{K} \xrightarrow{k_3} \text{K}$$

where B is benzophenone and K is cyclopentenone, and assuming a steady state, the Stern–Volmer expression:

$$\frac{\phi_0}{\phi} = 1 + \frac{k_2k_3[\text{K}]}{(k_\text{p} + k_\text{t})(k_{-2}[\text{B}] + k_3)}$$

may be derived. The constants k_p and k_t, $1{\cdot}36 \times 10^2\ \text{sec}^{-1}$ and $9{\cdot}1 \times 10^3\ \text{sec}^{-1}$, are now available from room-temperature measurements.[7c] The first-order decay rate of cyclopentenone is near $10^8\ \text{sec}^{-1}$,[1] and k_{-2} was taken as the diffusion rate, $10^{10}\ \text{M}^{-1}\ \text{sec}^{-1}$. A plot was obtained (Figure) with slope 7·3. From this, with the above values, the rate of energy transfer, k_2, is $6{\cdot}1 \times 10^5\ \text{M}^{-1}\ \text{sec}^{-1}$. This value clearly excludes the existence of a cyclopentenone triplet near or below that of benzophenone. Assuming that the rate of energy transfer is controlled only by the endothermicity, then the Boltzmann population distribution requires for the decrease in rate below diffusion control an endothermicity of about 6 kcal/mole. Since the triplet energy of benzophenone is 67·6 kcal/mole[7c] a value for the cyclopentenone triplet of near 73·6 kcal/mole results, in agreement with the sensitization experiments.[1] The quenching occurring in isopropyl alcohol solutions is therefore not an energy-transfer process. Presumably the benzophenone ketyl radical is acting as a hydrogen-transfer agent.[2c,8]

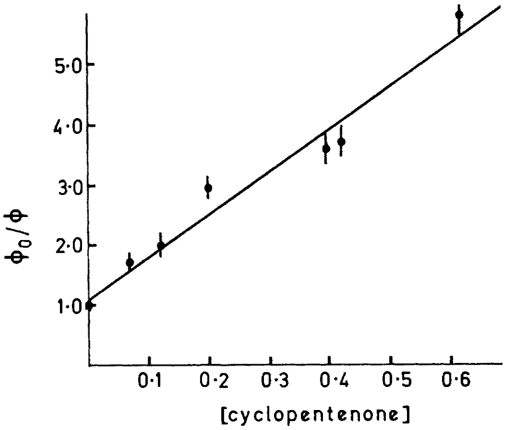

FIGURE. *Stern–Volmer quenching of benzophenone phosphorescence by cyclopentenone in carbon tetrachloride at 25°.*

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[1] P. de Mayo, J. P. Pete, and M. F. Tchir, *J. Amer. Chem. Soc.*, 1967, **89**, 5712; *Canad. J. Chem.*, 1968, **46**, 2535.

[2] (a) P. de Mayo, A. A. Nicholson, and M. F. Tchir, *Canad. J. Chem.*, 1970, **48**, 225; (b) R. L. Cargill, P. de Mayo, A. C. Miller, K. R. Neuberger, D. M. Pond, J. Saltiel, and M. F. Tchir, *Mol. Photochem.*, 1969, **1**, 301; (c) P. J. Wagner and D. J. Buchek, *J. Amer. Chem. Soc.*, 1969, **91**, 5090.

[3] J. L. Ruhlen and P. A. Leermakers, *J. Amer. Chem. Soc.*, 1966, **88**, 5671.

[4] A criticism made [N. J. Turro, J. C. Dalton, and D. S. Weiss in *Org. Photochem.*, 1969, **2**, 43] is in error. A slope has been confused with a ratio.

[5] B. Kirkiacharian, P. de Mayo, and A. A. Nicholson, *Mol. Photochem.*, 1970, **2**, 145.

[6] D. R. Kearns, G. Marsh, and K. Schaffner, *J. Chem. Phys.*, 1968, **49**, 3316; G. Marsh, D. R. Kearns, and K. Schaffner, *Helv. Chim. Acta*, 1968, **51**, 1890.

[7] (a) C. A. Parker, *Chem. Comm.*, 1968, 749; (b) W. D. K. Clark, A. D. Litt, and C. Steel, *J. Amer. Chem. Soc.*, 1969, **91**, 5413; (c) J. Saltiel, H. Curtis, and L. Metts, *ibid.*, 1970, **92**, 410.

[8] B. M. Monroe and S. A. Werner, *J. Amer. Chem. Soc.*, 1969, **91**, 450; J. G. Pacifici and G. Irick, *Tetrahedron Letters*, 1969, 2207.