

Short Communication

Arrhenius parameters for intermolecular triplet energy transfer from biacetyl to 1,3-butadiene

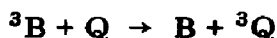
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1. Introduction

The kinetics of the intermolecular triplet electronic energy transfer from carbonyl compounds to π -bonded molecules have been studied extensively in recent years. However, studies of triplet energy transfer reactions have generally been confined to systems at a single temperature and the kinetics have been interpreted on the basis of rate constants at room temperature. In a number of investigations in the gas phase it has been demonstrated that the phosphorescence emitted by biacetyl can readily be quenched by various unsaturated compounds. The experimental observations in these studies have been adequately accounted for by the triplet-triplet energy transfer process



Triplet energy transfer appears to occur to 1,3-butadiene [1 - 3], *cis*- and *trans*-1,3-pentadiene [4], 2,3-dimethylbut-2-ene [1], styrene [1], ketene [5, 6] and various azoalkanes [7, 8].

Since the temperature effect on the lifetime of triplet biacetyl has recently been determined [9], studies of the temperature dependence of the quenching ability of added compounds are now possible. In this work measurements are described of the gas phase collisional quenching of triplet 3A_u biacetyl by 1,3-butadiene over a range of temperatures utilizing time-resolved laser-excited phosphorescence. The Arrhenius parameters derived should be of value in the understanding of the mechanism of the energy transfer process.

2. Experimental

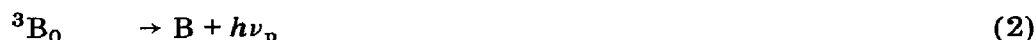
Triplet 3A_u biacetyl molecules were produced via intersystem crossing from the first excited singlet state 1A_u when biacetyl was irradiated close to the 0-0 band of the ${}^1A_u \leftarrow {}^1A_g$ absorption. The experimental arrangement was similar to that described previously [9]. An Electrophotonics flashlamp-pumped dye laser operating with Coumarin 2 gave radiation of wavelength

440 nm with a bandwidth of 1 nm. The pulsed output energy following attenuation with neutral density filters was approximately $2 \mu\text{J}$ and had a pulse duration of approximately $0.5 \mu\text{s}$. The laser beam was directed into the T-shaped Pyrex luminescence cell which was contained in a blackened furnace controlled to within $\pm 0.2^\circ\text{C}$. Phosphorescence was detected perpendicular to the incident radiation with an E.M.I. 9659 QB photomultiplier fitted with a 500 nm long-pass filter. The intensity-time record of the phosphorescence decay was displayed on an oscilloscope, photographed and analysed. Careful examination of the phosphorescence decay showed no evidence of non-exponentiality and lifetimes were determined with a typical reproducibility of better than 3%.

A grease-free mercury-free vacuum system was used for all the measurements. Pressure measurements were made using a mercury manometer coupled to a Pyrex spiral gauge. Biacetyl was purified as previously described [9] and 1,3-butadiene (Matheson Gas Products Research Grade) was bulb-to-bulb distilled on the vacuum line with the middle fraction being retained.

3. Results and discussion

The behaviour of the triplet state of biacetyl in the presence of 1,3-butadiene can be considered in terms of the following mechanism [9]:



In this mechanism, process (1) encompasses all photophysical processes prior to the attainment of thermalized triplet molecules (*i.e.* light absorption, intersystem crossing to the triplet state and vibrational equilibration in the triplet state).

Stern-Volmer plots of the measured lifetimes for each temperature studied are shown in Fig. 1. After the usual sequence of experiments was complete the lifetimes were remeasured at a low temperature to ensure that quenching by decomposition products had not interfered. To verify that the measured quenching rate constants were independent of biacetyl concentration the quenching rate was studied over a range of biacetyl concentrations from approximately 5×10^{-5} to $1.3 \times 10^{-3} \text{ mol l}^{-1}$. The quenching rate constants derived from the slopes of the Stern-Volmer plots are shown in Fig. 2 plotted in Arrhenius form and give

$$k_5(1,3\text{-butadiene}) = 10^{9.3 \pm 0.2} \exp\{-(2.3 \pm 0.2 \text{ kcal mol}^{-1})/RT\} \text{ l mol}^{-1} \text{ s}^{-1}$$

The value of the quenching rate constant at 25°C is in excellent agreement with previous estimates determined by relative phosphorescence emission yield techniques [1, 3].

Rate constants reported for triplet energy transfer from biacetyl to a variety of unsaturated compounds vary by more than a factor of 10^5 depend-

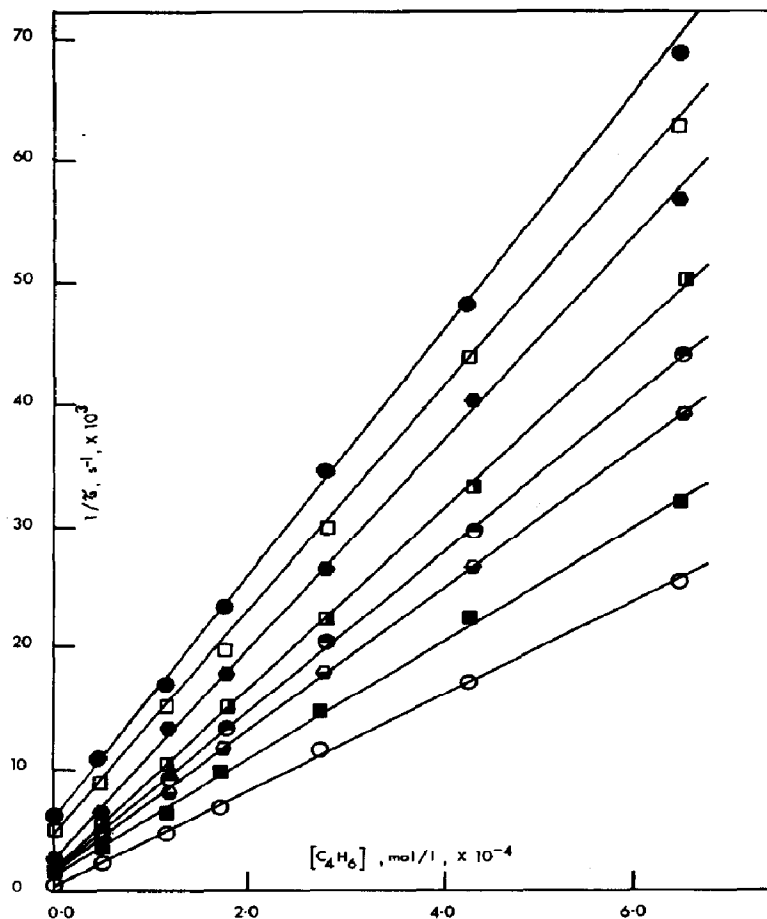


Fig. 1. Stern-Volmer plots of the inverse lifetime of the biacetyl triplet *vs.* the concentration of 1,3-butadiene at various temperatures: ○, 25 °C; ■, 44 °C; ◇, 61 °C; ●, 74 °C; ■, 84 °C; ●, 99 °C; □, 112 °C; ●, 123 °C.

ing on the nature of the acceptor molecule. Many of these changes can be rationalized in terms of the enthalpy change of the energy transfer reactions. Taking a value of 57.2 kcal for the 0-0 band of the ${}^3A_u \leftarrow {}^1A_g$ transition of biacetyl [10], reaction (5) is exothermic by about 4 kcal mol⁻¹ for the azoalkanes and the rate constant for quenching approaches the collision number. Similarly, for quenching of biacetyl phosphorescence in benzene solution, the quenching rate constant approaches the value expected for a diffusion-controlled reaction when the acceptor triplet energy is several kilocalories per mole below the triplet energy of biacetyl [11, 12]. Although there is good correlation between quenching rate constants and the exothermicity of the reaction there are considerable individual variations. Schmidt and Lee [2] have proposed that the probability of triplet energy transfer is also dependent on the extent of spectral overlap between biacetyl phosphorescence and the singlet-to-triplet absorption spectrum of the acceptor. However, for molecules with higher triplet energies than that of

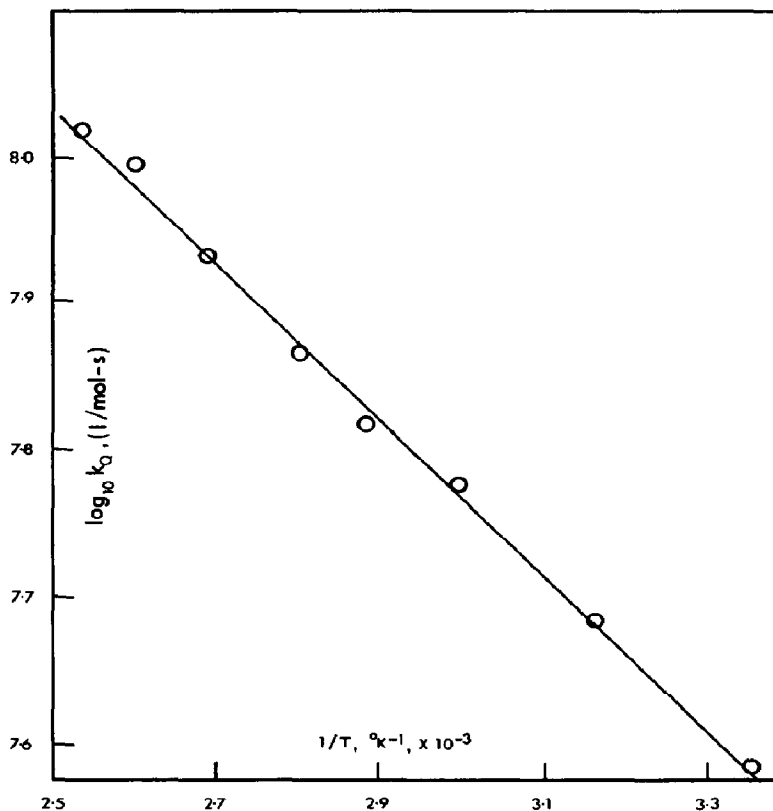


Fig. 2. Arrhenius plot of the quenching rate constant for the biacetyl triplet state by 1,3-butadiene.

biacetyl, quenching is much less efficient and it appears that the endothermicity of the reaction plays a significant role [1, 4]. The activation energy found in this work for the quenching of biacetyl triplets by 1,3-butadiene ($E_T = 59.6$ [13] and 59.8 [14] kcal mol^{-1}) is close to the enthalpy change of the triplet energy transfer process and suggests that the observed activation energy reflects the energy required to overcome the endothermicity of the reaction. This observation is consistent with the suggestion of Sandros [11] who has proposed that, for an endothermic triplet energy transfer reaction, the rate constant k_b is related to the rate constant k_f for the exothermic reverse reaction by the equation

$$k_b = k_f \exp(-\Delta E_T/RT)$$

where ΔE_T is the endothermicity of the reaction.

The pre-exponential factor lies in the range found for rate constants determined for exothermic energy transfer processes where there is no such energy barrier.

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