

Short Communication

Arrhenius parameters for the photocleavage of butan-2-one triplets

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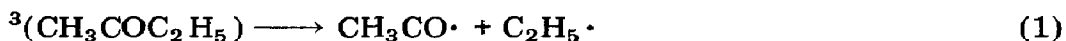
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The gas phase photochemistry of alkyl ketones which can only photodecompose by a Norrish type I mechanism has been the subject of several investigations. From these studies, it has been possible to obtain quantitative information on the fate of the excited molecules and to establish qualitative relationships between structural changes and photochemical behaviour [1]. However, since most of the rate constants have been obtained at a single temperature, there are very few Arrhenius parameters reported for the unimolecular bond cleavage of the excited molecules. The only reported Arrhenius parameters have been obtained by O'Neal and Larson for the photodecomposition of acetone triplets in the gas phase [2], and by Lissi *et al.* for the photochemistry of 4-methylpentan-2-one in n-hexane solution [3]. The Arrhenius parameters obtained in these studies are in considerable disagreement. The pre-exponential factors differ by a factor of nearly 10^6 (which is most unlikely for similar reactions) and the relative values of the activation energies are contrary to those expected from the selectivity shown by unsymmetric ketones where it is found that the less substituted α carbon cleaves much more slowly [1, 4]. In addition to the work of Lissi *et al.* [3], there are several other publications in which the effect of temperature upon the relative importance of type I and type II photoreactions has been reported [5]. Unfortunately, in these studies only quantum yields have been measured and the results do not allow the evaluation of Arrhenius parameters. Nevertheless, these results show that the importance of the cleavage increases when the temperature increases, indicating that the activation energy for the process is higher than that of the competitive intramolecular hydrogen abstraction. Since the knowledge of the Arrhenius parameters for the type I process is basic to the understanding of the mechanism by which this photoprocess takes place, and we can allow an estimate of the restriction imposed by the surface crossing involved [6], we decided to study the temperature effect upon the triplet lifetime of butan-2-one. This ketone was selected since: (i) the triplet lifetime is relatively large and can be measured by conventional methods; (ii) the main photoprocess from the triplet is the α bond cleavage; and (iii) at relatively low pressures the unimolecular

reaction from the triplet is in the high pressure limit [1].

The triplet lifetime of butan-2-one can be considered to be almost exclusively determined by the rate of reaction (1):



in the temperature range investigated [1]. The change in lifetime with temperature can then be equated to the change of k_1 with temperature, and these data can be employed to obtain the Arrhenius parameters of the unimolecular bond cleavage.

Mixtures of butan-2-one (35 Torr) and varying amounts of biacetyl (0.04 to 4 Torr) were introduced in a T-shaped, water-jacketed emission cell and irradiated with the 3130 Å band of a medium pressure mercury lamp (isolated with an Ealing TFP interference filter). The reagents were introduced from a higher pressure to improve the mixing. In some runs, propane was added to increase the total pressure. The green biacetyl emission was measured with a photomultiplier connected to a picoammeter. The amount of light absorbed by the biacetyl, as well as its emission when irradiated alone, was negligible and no correction had to be introduced due to these factors. The temperature range employed was 18 to 73 °C.

The change in biacetyl emission with biacetyl pressure at a given temperature can be directly related to the quenching of the thermalized butan-2-one triplet if: (i) the input of thermalized butan-2-one triplets is not modified by the biacetyl; (ii) the only state quenched by the biacetyl is the thermal triplet; and (iii) the efficiency of biacetyl emission is not dependent upon the biacetyl pressure.

These conditions were met by working at low intensities, constant total pressure and with $p_{\text{butanone}} \gg p_{\text{biacetyl}}$. Working at $p_{\text{butanone}} \gg p_{\text{biacetyl}}$ we can disregard the quenching of vibrationally excited butan-2-one triplets. Furthermore, we can also consider under these conditions that the quantum yield of thermalized butan-2-one triplets does not vary with biacetyl pressure owing to vibrational deactivation in the singlet or triplet manifold. Quenching of the excited singlet can be disregarded since the pressures of biacetyl employed are not enough to quench appreciably the ketone fluorescence even at room temperature [7].

Under the above-mentioned conditions eqn. (2) must hold:

$$1/I = K \{ 1 + (k_1/k_Q)(1/[\text{Biacetyl}]) \} \quad (2)$$

where I is the biacetyl emission intensity measured in arbitrary units; K is a constant at a given temperature; and k_Q is the specific rate constant for the quenching of thermalized triplets by biacetyl.

From a plot of $(1/I)$ against the inverse biacetyl pressure, the slope to intercept ratio provides the value of k_1/k_Q . In order to evaluate k_1 from this ratio, we considered that k_Q at 40 °C was equal to the rate of quenching of acetone triplets by biacetyl at the same temperature [8], and that it changes with temperature as $T^{3/2}$. The values of k_1 thus obtained are shown in an Arrhenius type plot in Fig. 1.

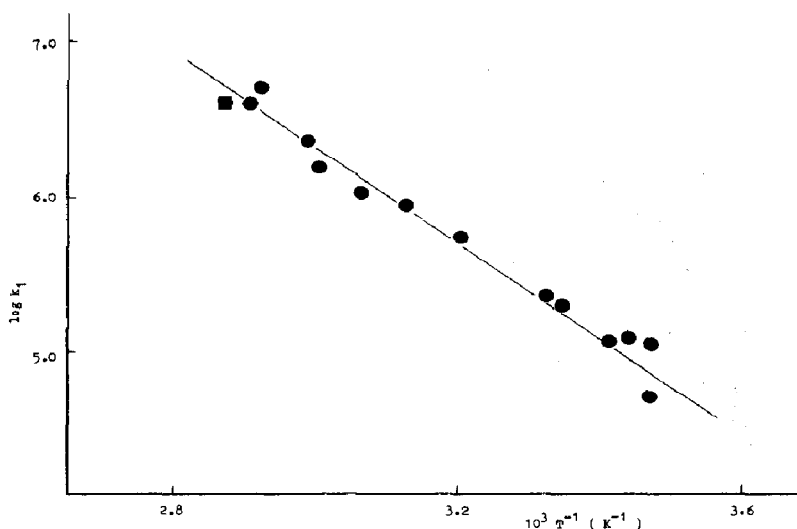


Fig. 1. Arrhenius plot for the thermal photocleavage of butan-2-one triplets. Butan-2-one pressure, 35 Torr; butan-2-one pressure, 35 Torr; propane pressure, 365 Torr.

In order to evaluate the influence of the total pressure upon the value of k_1 , some quenching experiments were carried out at higher values of total pressure. The result obtained at 73 °C and 400 Torr (35 Torr of butan-2-one plus propane) has been included in Fig. 1. We can conclude that any dependence of k_1 with total pressure lies within our experimental error. Furthermore, at lower temperatures, the pressure dependence of k_1 must be even less important [9]. This fact implies that we can consider our experimental values as those corresponding to the high pressure limit.

The data shown in Fig. 1 gives:

$$\log k_1 = (14.63 \pm 1.49) - (12,710 \pm 2150)/\Theta$$

(errors quoted represent 95% confidence limits). At room temperature the value of k_1 agrees with previous estimates [1].

The activation energy obtained (12.7 kcal/mol) is considerably higher than that reported by O'Neal and Larson for the α cleavage of acetone triplets (~ 10 kcal) [2]. These results are then contrary to those expected from the relative triplet lifetimes. On the other hand, the value for the activation energy obtained in the present work is similar to that reported by Lissi *et al.* for the bond cleavage in 4-methyl-pentan-2-one triplets (14.4 kcal/mol [3]).

The pre-exponential factor obtained can be considered as "normal" for a simple bond fission. This result indicates that, although there is no electronic correlation between the n, π^* triplet and the ground state photoproducts, these can be reached without significant restriction. This conclusion is in agreement with the description proposed by Dauben *et al.* for this type of process [6].

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