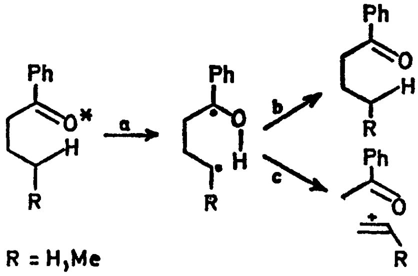
Arrhenius Parameters for Some Type II Photofragmentations of Aromatic Ketones

By J. C. SCAIANO*
(*Christopher Ingold Laboratories, University College, London, 20 Gordon Street, London* WC1H OAJ)
and J. GROTEWOLD and C. M. PREVITALI
(*Facultad de Farmacia y Bioquimica, Universidad de Buenos Aires, Junin* 956, *Buenos Aires, Argentina*)

Summary The Arrhenius parameters for the Type II photofragmentation of butyrophenone and valerophenone have been determined by studying the temperature dependence of the competition of these reactions with the quenching by penta-1,3-diene.

THE Type II photofragmentation is a subject of current interest in photochemistry.[1] Many of the studies in this field have involved aromatic ketones in the liquid phase. None of these studies has included the measurement of Arrhenius parameters. Pitts *et al.*[2] have studied the temperature dependence on the quantum yield of photofragmentation of butyrophenone. From a plot of log Φ *vs.* T^{-1} they determined a 'formal' activation energy of 2 kcal mol^{-1}; this can be taken as the temperature coefficient of the quantum yield of reaction, but not as its activation energy.

We have undertaken the determination energies and pre-exponential factors for the Type II photofragmentation of the triplet state of aromatic ketones in non-polar solutions. These parameters can be taken to correspond to a γ-hydrogen abstraction process, reaction (1a).



(1)

We report here the Arrhenius parameters for the first pair of compounds to be studied, namely, butyrophenone (R = H) and valerophenone (R = Me).

The rate constants at each temperature were determined from Stern–Volmer plots. The reactions were carried out in benzene solvent using a Hanovia 125 W medium-pressure mercury arc as light source. The samples were contained in matched Pyrex tubes and the conversions kept below 2%. The ratios of quantum yields were determined by g.l.c. analysis of acetophenone (against n-dodecane as a standard) for several concentrations of penta-1,3-diene.

The reactions were studied from 5—73° and the rate constants determined at 10—15° intervals. Then, $\log(k_q\tau)$ was plotted against T^{-1} and fitted by least squares. The following expressions were obtained:

$$\log(k_q\tau/1\ \text{mol}^{-1})_B = (0\cdot15 \pm 0\cdot30) + (3600 \pm 600)/2\cdot3\ \boldsymbol{R}T$$

$$\log(k_q\tau/1\ \text{mol}^{-1})_V = (0\cdot25 \pm 0\cdot30) + (1650 \pm 500)/2\cdot3\ \boldsymbol{R}T$$

where $\boldsymbol{R}$ is in cal mol^{-1} K^{-1} and the subscripts B and V stand for butyrophenone and valerophenone, respectively. k_q was assumed to follow an Arrhenius temperature dependence, with E_a being obtained by graphical derivation of the modified Debye's equation,[3] equation (3).

$$E_a = -\boldsymbol{R}\frac{\partial[\ln(8\boldsymbol{R}T/3000\eta)]}{\partial(T^{-1})} = -\boldsymbol{R}\frac{\partial[\ln(T/\eta)]}{\partial(T^{-1})} \qquad (3)$$

Using this activation and assuming $k_q = 5 \times 10^9\ 1\ \text{mol}^{-1}\ \text{s}^{-1}$ at 20° (in order to be consistent with previous studies) the following expression was derived:

$$\log(k_q/1\ \text{mol}^{-1}\ \text{s}^{-1}) = 11\cdot95 - (3050/2\cdot3\ \boldsymbol{R}T)$$

therefore,

$$(k_{1a})_B = 10^{11\cdot80} \times \exp(-6650/\boldsymbol{R}T)\ \text{s}^{-1}$$

$$(k_{1a})_V = 10^{11\cdot70} \times \exp(-4700/\boldsymbol{R}T)\ \text{s}^{-1}$$

At room temperature the expressions shown above agree well with rate constants determined in other laboratories.[4] The difference in activation energies between the two ketones is probably a consequence of the difference in bond energies of the γ–hydrogens. The A-factors deserve little comment since both seem reasonable values for reactions of this type. Estimation of the 'expected' activation energies using semiempirical methods[5] suggests that the six-centre-abstraction-ring must be quite unstrained.

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