Tetrahedron Letters No.34, pp. 3029-3032, 1970. Pergamon Press. Printed in Great Britain.

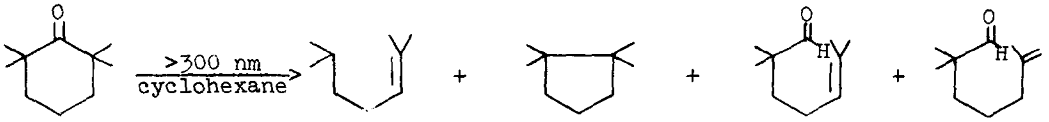
EVIDENCE FOR THE INVOLVEMENT OF TWO EXCITED STATES IN THE PHOTOLYSIS OF A CYCLIC KETONE[1]

James M. Beard[2] and Richard H. Eastman
Department of Chemistry
Stanford University, Stanford, California 94305

(Received in USA 12 June 1970; received in UK for publication 22 June 1970)

Two of the best known photoreactions of saturated organic ketones are the Norrish Type I and Type II cleavages. Although much research[3] has been done on the mechanisms of these reactions, relatively little is known about the excited states responsible for the Norrish Type I reaction in solution. Yang and Feit[4] have reported evidence for the involvement of two excited states in the Norrish Type I cleavage of a series of *t*-butyl alkyl ketones in hexane solution. However, in a series of substituted cyclohexanones Wagner and Spoerke[5] concluded that α-cleavage occurred exclusively from the triplet state. In this communication we would like to report the results of our investigation into the excited states involved in the Norrish Type I cleavage of 2,2,6,6-tetramethylcyclohexanone (1).

The photolysis of ketone 1 in cyclohexane solution in Pyrex leads to four products: 2,6-dimethyl-2-heptene (2), 1,1,2,2-tetramethylcyclopentane (3), 2,2,6-trimethyl-5-heptenal (4), and 2,2,6-trimethyl-6-heptenal (5). Product 2 was previously identified by Starr and Eastman,[6] and the structures of products 3 and 4 were assigned using elementary analysis and spectral evidence. Structure 5 is based on spectral evidence alone.



1 2 (3%) 3 (1%) 4 (85%) 5 (11%)

Quenching studies were carried out using 1,3-cyclohexadiene as the quencher. For analytical reasons, the most reliable quenching data are those for aldehyde 4, which is shown in Figure 1. The other products give a similar plot. The

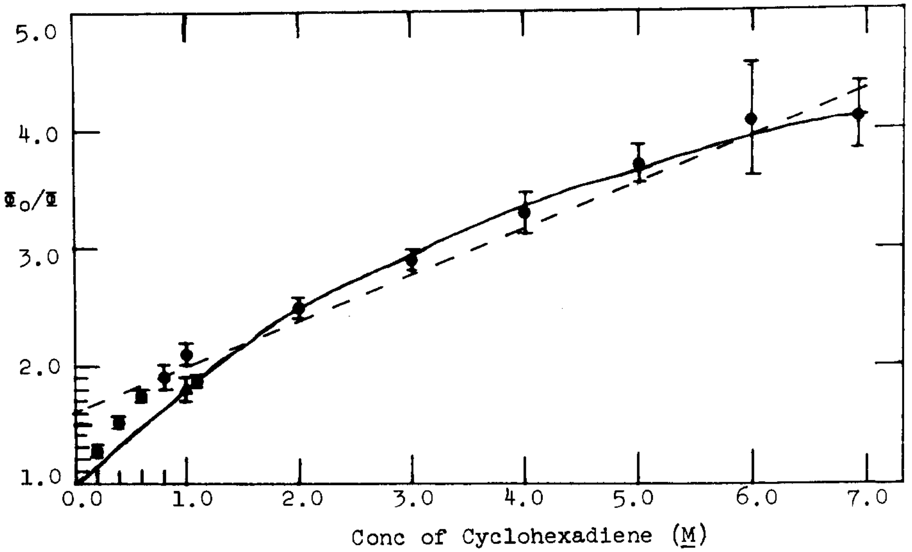


Figure 1. Stern-Volmer Plot for the Quenching of the Appearance of Aldehyde 4 with 1,3-Cyclohexadiene. The solid line is fitted to eq 2 and the broken line is the least squares straight line. The triangular symbol (▲) indicates an independent experiment.

points from 0.2 M cyclohexadiene to 1.0 M cyclohexadiene were obtained with samples containing 0.2 M ketone 1; those from 1.1 M cyclohexadiene to 7.0 M cyclohexadiene with samples containing 0.8 M ketone 1. The higher concentration of ketone 1 was used to nullify any absorption by cyclohexadiene. Samples of ketone 1 and cyclohexadiene plus n-decane as an internal standard were degassed, and sealed. The 0.2 M samples were photolyzed for one hour, the 0.8 M samples for four hours, both at 30°in a merry-go-round apparatus[7] with filtering[8] to isolate the 313 nm band; and they were then analyzed by gas liquid partition chromatography.

Least squares analysis of the data gives a line of slope 0.419 and y-intercept 1.48, and standard deviation ±0.16. The Stern-Volmer equation, $(\Phi_0/\Phi) = 1 + k_q\tau[Q]$ (1), requires that the y-intercept be unity and the observed y-intercept of 1.48 is well outside experimental uncertainty. (The best line having an imposed y-intercept of unity has standard deviation ±0.37.)

The simple Stern-Volmer expression (1) applies only when the product upon which the quantum yield is based is formed from a single excited state that undergoes energy transfer to the quencher. For the case of two states, one quenched and one not, yielding the product, the following expression may be derived:

$$\frac{\Phi_0}{\Phi} = \frac{1 + k_q \tau[Q]}{1 + k_q \alpha[Q]} , \qquad (2)$$

wherein τ is the lifetime of the quenchable state in the absence of quencher and

$$\alpha = \frac{1}{k_2 + k_d + \frac{k_2}{k_1} k_i} .$$

In the latter expression, k_2 is the rate constant for formation of the product from the quenchable state, k_d is the rate constant for all paths of deactivation of the quenchable state other than by energy transfer to quencher (Q), k_1 is the rate constant for the production of product from the unquenchable state, and k_i is the rate constant for the production of the quenchable from the unquenchable state. Commonly, k_i is the rate constant for intersystem crossing.

Attempts to fit all of the data on quenching to equation 2 failed because of the discontinuity (Figure 1) in the region near 1 M quencher concentration where the concentration of ketone 1 was changed from 0.2 M to 0.8 M to accommodate growing absorption by quencher. However, the data for quenching in the 0.8 M solutions of ketone fit equation 2 having $k_q\tau = 1.08$ and $k_q\alpha = 1.53$ with a standard deviation of only ± 0.08 (solid curve in Fig. 1).[9] The fit is taken as strong evidence that two excited states are involved in the photochemistry of ketone 1 , in contrast to the results of Wagner[3] for 2,2- and 2,6-dimethylcyclohexanone.

If one assumes a diffusion-controlled value for k_q of 8.1×10^9 l mole^{-1} sec^{-1}, the data for the photolysis of ketone 1 yield a lifetime of the order of 1.3×10^{-10} sec for the quenchable state, a value that fits well into the series of lifetimes reported by Wagner and Spoerke.[5] This exceedingly short lifetime suggests that the n,π* excited state has become very reactive with respect to α-cleavage and that in this case cleavage may have a reasonable probability occurring within the lifetime of the singlet.

Acknowledgments. The authors are grateful for helpful discussions with Drs. J. I. Brauman, L. J. Altman, and L. M. Stephenson.

REFERENCES

1. Abstracted from the Ph.D. dissertation of J.M.B.
2. NSF Trainee, 1967-69.
3. J. G. Calvert and J. N. Pitts, "Photochemistry", J. Wiley and Sons, Inc., New York, 1966, pp 377-427; N. J. Turro, "Molecular Photochemistry", W. A. Benjamin, Inc., New York, 1965, ch 9; R. O. Kan, "Organic Photochemistry", McGraw-Hill Book Co., San Francisco, 1966, ch 3; J. S. Swenton, *J. Chem. Ed.*, **46**, 217 (1969).
4. N. C. Yang and E. D. Feit, *J. Amer. Chem. Soc.*, **90**, 504 (1968).
5. P. J. Wagner and R. W. Spoerke, *ibid.*, **91**, 4437 (1969).
6. J. F. Starr and R. H. Eastman, *J. Org. Chem.*, **31**, 1393 (1966).
7. R. S. H. Liu, N. J. Turro and G. S. Hammond, *J. Amer. Chem. Soc.*, **87**, 3406 (1965).
8. The filter was 8 mm of 0.002 *M* potassium chromate in one percent aqueous potassium carbonate.
9. The least-squares line (broken in Fig. 1) for the data has the wrong orientation and a y-intercept of 1.61 that is well outside experimental error. Forcing the line to a y-intercept of unity more than doubles the standard deviation.