Tetrahedron Letters No. 27, pp 2261 - 2264, 1975. Pergamon Press. Printed in Great Britain.

ENERGY MIGRATION. THE ENERGY HOPPING AND SELF-QUENCHING REACTION INVOLVING CARBONYL CHROMOPHORES

Gary Schuster and Nicholas J. Turro*
Chemistry Department, Columbia University, New York, New York 10027

(Received in USA 18 March 1975; received in UK for publication 20 May 1975)

Introduction

The interaction of an electronically excited chromophore with a ground state chromophore of the same type is important in many photochemical processes.[1] The carbonyl chromophore, because of its involvement in many mechanistic and practical photochemical processes, has played a leading role in the development of photochemical concepts. We report here the results of experiments designed to study the interaction of one electronically excited carbonyl chromophore with a ground state carbonyl group. This study takes advantage of the unique abilities of chemiluminescence techniques.

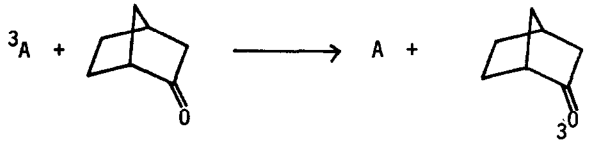
Results

The interaction of an electronically excited carbonyl with a ground state carbonyl can lead to three general types of results: (a) chemical reaction[2]; (b) excitation transfer[3] and (c) physical quenching[4]. The technique employed in this study involves generation of triplet acetone (^3A) by thermolysis of tetramethyl-1,2-dioxetane (TMD) and quenching of the phosphorescence of acetone by various ketones. The latter ketones were selected so that the triplet states (^3K) were short lived and therefore unlikely to participate in energy transfer processes. Thus, quenching of ^3A by one of these ketones to produce ^3K is irreversible and results in a "quench" of ^3A. Under such conditions, the intensity of acetone phosphorescence should follow simple Stern-Volmer kinetics (eq. 1).

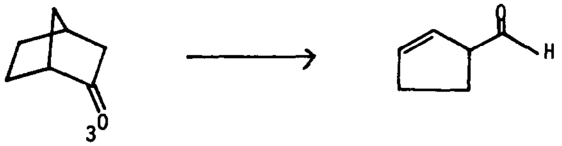
$$\frac{I_p^o}{I_p} = 1 + k_q\tau_T[Q] \tag{1}$$

A typical system is TMD and norcamphor (NC) in acetonitrile solvent. The triplet of the latter is very short lived and can be quenched only with high concentrations of the best triplet quenchers.[5] The short triplet lifetime of NC is due to a rapid α-cleavage reaction from T_1. Experimentally, we observe the formation of the expected enal product from triplet NC when TMD is thermolyzed

$$\text{TMD} \longrightarrow {}^3\text{A} + \text{A} \tag{2}$$



(4)



(5)

in the presence of NC, providing direct evidence for energy migration or hopping from ^{3}A to NC. Table I summarizes data for the quenching of acetone phosphorescence by a variety of ketones. The lifetime of ^{3}A under the reaction conditions was measured by single photon counting and is equal to 10×10^{-6} sec. Based on this value of τ_T, absolute values of k_q may be evaluated (Table 1).

Similarly, the self-quenching of acetone triplet was studied by chemiluminescent techniques. In the range 1 to 13 _M_ acetone, no effect of acetone concentration on the emission of ^{3}A was observed. An upper limit of 10^3 M^{-1} sec^{-1} for the self-quenching of triplet acetone may be derived from the experimental uncertainty.

Discussion

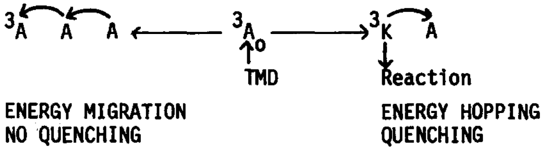
The values of k_q for quenching of ^{3}A by the ketones studied vary by less than a factor of two from 1×10^6 M^{-1} sec^{-1}. The near identity of k_q for carbonyl quenchers of varying structures suggests that (a) steric effects are unimportant in the quenching step and (b) a common quenching mechanism is available to all of the ketones studied. The observation that norbornane quenches ^{3}A with a rate constant at _ca._ one hundreth the rate of the ketones indicates that the quenching interaction is with the carbonyl group of the quencher and not the hydrocarbon portion.

The rate constant for energy hopping from acetone triplet to acetone has been estimated[3] to be ~3×10^6 M^{-1} sec^{-1}. On the basis of the above consideration we conclude that the mechanism of quenching of ^3A by ketones is irreversible triplet energy transfer. The rate of the energy transfer process is relatively slow and may reflect the difference between the ground and excited state geometry of the carbonyl chromophore. It is interesting to note that in the case of acetone, unlike acetophenone[1e], self-quenching is negligible even though migration is substantial!

Summary (Scheme I)

We provide evidence here for energy hopping from an excited ketone triplet (^3A) to ground state ketones (K). The process is irreversible and results in quenching when the acceptor ketone possesses a shorter triplet lifetime than the donor triplet. The process is highly reversible in the case of acetone triplet to acetone, and as a result no self-quenching is observed.

Scheme I



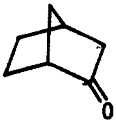
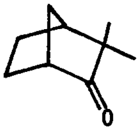
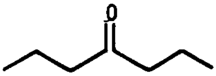
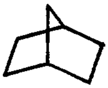
Acknowledgement

The authors at Columbia University wish to thank the Air Force Office of Scientific Research (Grant AFOSR=74-2589B) and the National Science Foundation (Grant NSF-GP-2660x and NSF-GP-40330x) for their generous support of this research. G.S. wishes to thank NIH for a postdoctoral fellowship.

References

1. (a) D.I. Schuster and M.D. Goldstein, J.Amer.Chem.Soc., 95, 986 (1973);
   (b) C.D. De Boer and R.H. Schlessinger, J.Amer.Chem.Soc., 94, 655 (1972);
   (c) J.A. Bell and H. Linschitz, J.Amer.Chem.Soc., 85, 528 (1963);
   (d) O.L. Chapman and G. Wampfler, J.Amer.Chem.Soc., 91, 5390 (1969);
   (e) L. Giering, M. Berger and C. Steel, J.Amer.Chem.Soc., 96, 953 (1974).
2. J.T. Przybytek, S.P. Singh and J. Kagan, Chem.Commun., 1224 (1969).
3. P. Lechtken and N.J. Turro, Angew.Chem.Internat.Ed., 12, 314 (1973).
4. G. Porter, S.K. Degra, R.O. Loufty, S.E. Suganori and R.W. Yip, Trans.Farad.Soc., 69, 1462 (1973).
5. P. Yates, Pure Appl.Chem., 16, 93 (1968).

TABLE I. Quenching of Acetone Triplets by Ground State Ketones[a]

Quencher	$k_q\tau_t^{(b)}(M^{-1})$	$k_q(M^{-1}\ sec^{-1})$
$(CH_3)_2CO$	<0.1	$<10^3$
	15	1.3×10^6
	13	1.1×10^6
	8	0.7×10^6
	12	1.1×10^6
	0.12	$<1\times10^4$

(a) Acetone triplets generated by thermolysis (52°) of TMD ($\sim10^{-5}$ M) in nitrogen purged acetonitrile solution.

(b) From equation 1. Stern-Volmer slopes determined from at least 9 points. Slopes were linear within a 95% confidence limit. Standard deviation at maximum = 10%.