Tetrahedron Letters Vol. 22, pp 517 - 520
0040-4039/81/0201-0517$02.00/0

QUENCHING OF AROMATIC KETONE PHOSPHORESCENCE BY STERICALLY HINDERED ALKENES

Utam Maharaj and Mitchell A. Winnik*
Lash Miller Laboratories, Department
of Chemistry, and Erindale College,
University of Toronto,
Toronto, Ontario M5S 1A1

Abstract:
The deactivation of the excited states of triplet ketones by sterically hindered alkenes results in lower rate constants (usually due to increased activation energies) than by relatively unhindered alkenes.

The deactivation rate constant, k_{ir}, of the excited triplet states of ketones by alkenes increases with the electron donating ability of the quencher[1]. This is due to the intermediacy of an exciplex[1] which is stabilized by significant electron transfer from olefin to excited ketone. Experimental and theoretical studies[2,3] have indicated that for quenching to occur the electron rich species must approach the half vacant n-orbital on the oxygen of the excited ketone. Bulky groups on the ketone which prohibit this approach[2] cause a lowering of reactivity. On the other hand, steric hindrance[4,5] on the olefin quencher has been reported not to show an influence on the reaction rate constant. This finding has been borne out for the series of alkenes[4] and enol ethers[5]. We have studied the triplet quenching of an aromatic ketone by sterically hindered alkenes and compared its reactivity to that of relatively unhindered alkenes. Activation energies and A-factors have been obtained for these reactions.

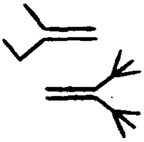
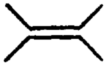
The ketone we have studied is the p-methyl carboxylate of benzophenone, the photochemistry and photophysics of which resemble that of benzophenone. Dilute (1.5×10^{-3} molar) solutions of the ketone with varying concentrations of alkene were made up in CCl_4[6], degassed by five successive freeze-pump-thaw cycles[6]; and the phosphorescence lifetimes of the ketone, measured by flash photolysis[6]. The lifetimes obtained were treated by the modified Stern-Volmer equation $1/\tau = 1/\tau_o + k_{ir}[Q]$, and k_{ir} determined by many (typically 10 - 15) temperatures[6] in the range -20°C to 100°C. Arrhenius plots yielded A-factors and activation energies which we report in the Table along with the rate constants at room temperature.

Unlike previous reports[4,5], our results clearly show that in each pair of alkenes bulky substituents cause significant lowering of reactivity, and one notes reductions in k_{ir} by factors of ca. 4 for 1,1- and trans-1,2-disubstituted, ca. 7 for cis-1,2-disubstituted, and ca. 10 for tetrasubstituted alkenes.

From our Arrhenius studies we can obtain a deeper understanding of what factors are responsible for the reduced reactivity of the sterically hindered olefins. With the exception of cis-1,2-ditert-butyl ethylene the decreased reactivity of the hindered alkenes is due to an increase in the activation energy over that for the unhindered alkene[7] of the same substitutions; however, there is essentially no change in A-factor. For example, the drop in reactivity of adamantylidene adamantane compared with tetramethylethylene[7] is due to a large increase in E_a, from ca. 0.15 to 2.11 kcal/mole, but the A-factors for both reactions are roughly the same. When one obtains the same A-factor for a pair of reactants undergoing the same reaction, it implies that the mechanism and the reaction geometries are the same. In the pairs of reactants that we have studied, the effect of cis-1,2 substitution is found to be quite different. The decreased reactivity of cis-1,2-ditert-butylethylene compared to the cis-2-pentene[7] is due to a substantial drop in the A-factor, and in fact we even observe a drop in the activation energy for this reaction.

Acknowledgements: The authors thank the Natural Sciences and Engineering Research Council Canada for its financial support, Professor P. A. Schaap of Wayne State University for a sample of adamantylidene-adamantane, and Professor T. T. Tidwell of the University of Toronto for samples of the tert-butyl ethylenes.

Table: Rate Constants and Arrhenius Parameters for the Quenching of C_1^{*3} by Various Alkenes[a]

Alkene	$k_{ir}^{25°C}, M^{-1}s^{-1}$	A-factor, $M^{-1}s^{-1}$	E_a, kcal/mol
	5.4×10^7	2.0×10^8	0.75 ± 0.07
	1.6×10^7	1.7×10^8	1.40 ± 0.07
	7.2×10^7	1.6×10^8	0.50 ± 0.04
	1.8×10^7	0.8×10^8	0.88 ± 0.06
	1.0×10^8	2.1×10^8	0.42 ± 0.10
	1.5×10^7	2.0×10^7	0.19 ± 0.05
 [b]	1.6×10^9	2.6×10^9	0.15 ± 0.17
A=A [c]	1.5×10^8	5.1×10^9	2.11 ± 0.3

a. C_1 is 4-carboxymethyl benzophenone. Experiments in carbon tetrachloride at -20° to 100°, with rate constants corrected for changes in solvent density[8].

b. Arrhenius parameters obtained from Arrhenius plot over the temperature range 40 - 100°C.

c. Adamantylidene-adamantane

References:

1. R. O. Loutfy, S. K. Dogra, and R. W. Yip, Can. J. Chem., 1979, 57, 342-347, and references therein.
2. N. C. Yang, M. H. Hui, D. M. Shold, N. J. Turro, R. R. Hautala, K. Dawes and J. C. Dalton, J. Amer. Chem. Soc., 1977, 99, 3023-3033.
3. a) U. Maharaj, I. G. Csizmadia and M. A. Winnik, J. Amer. Chem. Soc., 1977, 99, 946-948;
   b) K. Morokuma, G. H. Neems and S. Yamabe, Tet. Lett., 1977, 767-770;
   c) R. M. Wilson, R. Outcalt, and H. H. Jaffe, J. Amer. Chem. Soc., 1978, 100, 301-302.
4. a) A. Gupta and G. S. Hammond, J. Amer. Chem. Soc., 1976, 98, 1218-1223;
   b) I. E. Kochevar and P. J. Wagner, J. Amer. Chem. Soc., 1972, 94, 3859-3865.
5. N. E. Schore and N. J. Turro, J. Amer. Chem. Soc., 1975, 97, 2482-2488.
6. M. A. Winnik and U. Maharaj, Macromolecules, 1979, 12, 902-905.
7. A systematic study of the quenching of C_1^{*3} by the unhindered alkenes will be published elsewhere.
8. J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds", VI pp 224, VII pp184 and 434, Elsevier, New York, 1965.

(Received in USA 26 August 1980)