

THE TRIPLET STATE OF KETONES IN SOLUTION:  
QUENCHING OF TRIPLET ACETONE BY OLEFINS

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The formation of complexes between triplet excited and ground state molecules (triplet exciplexes) has attracted much interest, particularly in connection with the quenching of triplet ketones by amines<sup>2</sup>, olefins<sup>3</sup>, aromatic and aliphatic hydrocarbons<sup>4</sup>. A considerable body of evidence has given direct support for the intermediacy of a charge-transfer (CT) complex, ( $A^-B^+$ ), in many such systems<sup>2,3</sup>.

As part of our study of triplet ketone reactivity in solution<sup>4b</sup> by various pulsed techniques, we have measured rate constants for the quenching ( $k_q$ ) of triplet acetone<sup>5</sup> in order to obtain further insight into the interaction between triplet ketone and olefins. We found a linear relation between  $\log k_q$  and IP, the ionization potential of electron-rich olefins, as well as with  $E_{1/2}^{red}$ , the half-wave reduction potential of electron-deficient olefins, and we wish to report such correlations.

The decay of triplet acetone in degassed acetonitrile solutions was measured by the flash emission technique described earlier<sup>5</sup>. The rate constants for quenching ( $k_q$ ) of triplet acetone by a series of electron-rich and electron-deficient olefins along with relevant values for quenching of triplet butyrophenone and benzophenone<sup>3a</sup> are recorded in Table I.

We note from the results that (a) for a given olefin quencher  $k_q$  does not decrease with  $E_T$  of sensitizer as required by the commonly accepted triplet energy transfer mechanism, and (b)  $\log k_q$  does not correlate with the ionization potential (IP) of all of the quenchers. Let us consider the possibility of CT complex formation in light of the quenching results and with regard to the direction of charge transfer. Klein et al<sup>6</sup> developed a model in which the formation rate of this CT complex was considered as the rate determining step in the excitation quenching. According to this model the quenching rate constant ( $k_q$ ) can be related to the ionization potential of the donor ( $IP_D$ ) and electron affinity of the acceptor ( $EA_A$ ) by the following expression:

$$\ln k_q \approx -(IP_D - EA_A - C - P - E_T)/RT \quad (1)$$

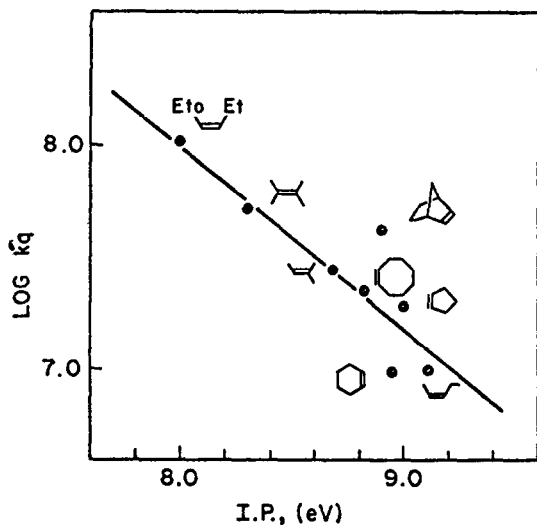


FIGURE 1: Plot of  $\log k_q$  for acetone triplet against the ionization potential of electron-rich olefins

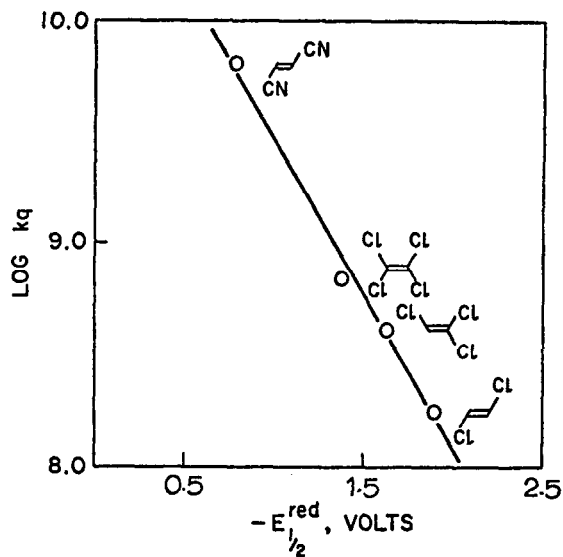


FIGURE 2: Plot of  $\log k_q$  for acetone and the half-wave reduction potential of electron-deficient olefins

TABLE 1: Quenching rate constants of acetone, butyrophenone and benzophenone triplet by substituted olefins

No.	Quencher	IP <sup>a</sup> eV	Sensitizer <sup>b</sup>		
			Acetone (E <sub>T</sub> =3.36eV) k <sub>q</sub> (M <sup>-1</sup> s <sup>-1</sup> ) × 10 <sup>7</sup>	Butyrophenone <sup>b</sup> (E <sub>T</sub> =3.13eV) k <sub>q</sub> (M <sup>-1</sup> s <sup>-1</sup> ) × 10 <sup>7</sup>	Benzophenone <sup>b</sup> (E <sub>T</sub> =2.97eV) k <sub>q</sub> (M <sup>-1</sup> s <sup>-1</sup> ) × 10 <sup>7</sup>
<u>Electron-rich olefins</u>					
1.	1-Ethoxy-1-butene	8.00	11.0	-	-
2.	2,3-Dimethyl-2-butene	8.30	5.1	46.0	89.5
3.	2-Methyl-2-butene	8.68	2.8	14.0	36.0
4.	Cyclo-octene	8.82	2.2	8.2	-
5.	Cyclo-hexene	8.95	1.0	4.2	5.7
6.	Norbornene	8.95	4.3	3.7	4.0
7.	Cyclopentene	9.01	1.9	5.2	-
8.	cis-2-Pentene	9.11	1.0	5.1	8.0
<u>Electron-deficient olefins</u>					
9.	Fumaronitrile (-0.78) <sup>c</sup>	11.0	650.0	580	120
10.	Tetrachloroethylene (-1.38)	9.32	68.5	145	-
11.	Trichloroethylene (-1.64)	9.45	42.0	72	-
12.	trans-Dichloroethylene (-1.90)	9.66	18.0	40	1.3

a. L. G. Christophorou, Atomic and Molecular radiation Physics. Edited by J. B. Birks and S. P. McGlynn. Wiley Interscience, 1971.

b. See reference 3a.

c. Half-wave reduction potentials, the values given have been converted to acetonitrile as solvent. C. K. Mann and K. K. Barnes, "Electrochemical Reactions in non-aqueous systems", Marcel Dekker, New York, 1970

where  $C$  is the Coulomb energy and  $P$  is the polarization energy of the separated charges.  $E_T$  represents the excitation energy. For acetone, correlation between  $\log k_q$  and IP of electron-rich olefins was found, see Figure 1, similar to that reported earlier by Wagner<sup>3a</sup>. However, the slope,  $-0.072$  mole/Kcal, is higher than that for butyrophenone ( $-0.047$ ) and for benzophenone ( $-0.036$ ) indicating a greater sensitivity of the acetone triplet to IP. On the other hand, correlation between  $\log k_q$  of triplet acetone and the reduction potential ( $E_{1/2}^{\text{red}}$ ) of chloroethylenes (electron-deficient olefins), see Figure 2, was found. The quenching of triplet acetone in this case appears to involve charge transfer from the excited ketone to the quenching olefin. The slope,  $0.06$  mole/Kcal, again is slightly greater than that for butyrophenone quenching by chloroethylenes ( $0.045$  mole/Kcal).

Values of  $\log k_q$  for quenching of a series of triplet ketones, having an  $n, \pi^*$  or  $\pi, \pi^*$  lowest triplet state, with a constant donor olefin, 2,3-dimethyl-2-butene, are given in Table II, along with the available triplet energies and half-wave reduction potentials of the ketones. The correlation between  $\log k_q$  and the excited ketone accepting ability term,  $-(E_{1/2}^{\text{red}} + E_T)_k$  is given in Figure 3. The nature of the excited state has apparently no effect on the course of the quenching. It is the electron affinity of the excited ketone which determines the rate of quenching by a given donor; this is consistent with Eq. 1. The slope,  $-0.657$  mole/Kcal, is much greater than that found by Cohen and Guttenplan<sup>7</sup> for quenching of triplet ketones by triethylamine of  $-0.25$  mole/Kcal.

In conclusion all of the qualitative features of the quenching of triplet ketones by olefins can be simply interpreted in terms of initial formation of triplet exciplex with partial charge transfer character.

TABLE II: Quenching of triplet ketones by 2,3-dimethyl-2-butene

Sensitizer	Lowest Triplet	$E_T, \text{eV}$ <sup>a</sup>	$-E_{1/2}^{\text{red}}, \text{Volts}$ <sup>a</sup> vs Ag/AgCl	$-(E_{1/2}^{\text{red}} + E_T), \text{eV}$	$k_q \text{ M}^{-1} \text{ s}^{-1}$ $10^7$
1. 2-Acetylnaphthalene	$\pi, \pi^*$	2.59 <sup>b</sup>	1.63 <sup>c</sup>	-0.96	0.28
2. 4-Benzoyl Biphenyl	$\pi, \pi^*$	2.58 <sup>b</sup>	1.60 <sup>d</sup>	-0.98	0.52
3. Acetone	$n, \pi^*$	3.36	2.31	-1.05	5.10
4. Butyrophenone	$n, \pi^*$	3.13	2.03	-1.10	46.0
5. Benzophenone	$n, \pi^*$	2.97	1.84	-1.13	89.5

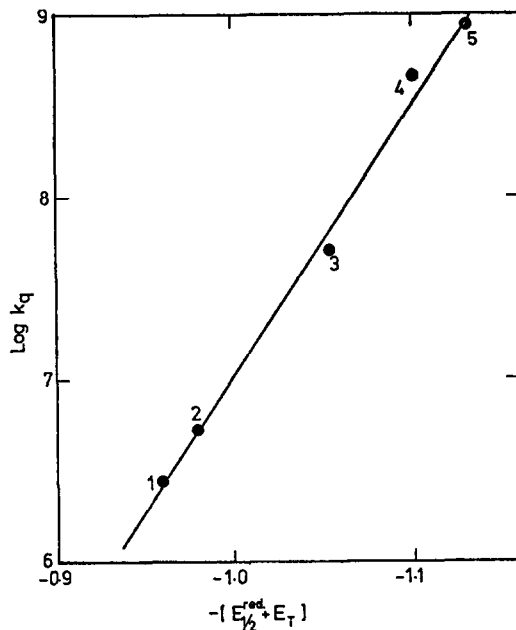
a. Rafik O. Loutfy and Raouf O. Loutfy, *J. Phys. Chem.*, **76**, 1650 (1972).

b. P. S. Egel and B. M. Monroe, *Adv. Photochem.* **8**, 302 (1970).

c. I. Kolthoff and J. J. Lingane, "Polarography" Volume 2, p.687, Wiley Interscience, New York (1952).

d. I. B. Rashkov, Tz. G. Popov, Gr. S. Michailov, I. M. Papyotov and A. Z. Trifonov, *Monatshefte fur Chemie*, **101**, 1797 (1970).

FIGURE 3: Plot of  $\log k_q$  for quenching of triplet ketones by tetramethylethylene vs triplet energy minus reduction potential of the ketones. Numbers refer to compounds in Table II.



#### REFERENCES:

- 1.a. Present address: Xerox Research Centre of Canada Ltd., 2480 Dunwin Drive, Mississauga, Ontario L5L 1J9, Canada.
- b. NRC Postdoctoral Fellow.
- 2.a. S. G. Cohen, A. Parola and G. H. Parsons, *Chem. Rev.*, **73**, 141 (1973).
- b. R. O. Loutfy, R. W. Yip, Y. L. Chow and L. K. Magdzinski, *Can. J. Chem.*, **50**, 3426 (1972).
- c. R. O. Loutfy and R. O. Loutfy, *Can. J. Chem.*, **50**, 4052 (1972).
- 3.a. P. J. Wagner and I. H. Kochevar, *J. Am. Chem. Soc.*, **94**, 3859 (1972).
- b. R. A. Caldwell, G. W. Sovocool and R. P. Gajewski, *ibid*, **95**, 2549 (1973).
- 4.a. D. I. Schuster, T. M. Weil and A. M. Halpern, *J. Am. Chem. Soc.*, **94**, 8248 (1972).
- b. R. O. Loutfy and R. W. Yip, *Can. J. Chem.*, **51**, 1881 (1973). Other references therein.
- c. L. Giering, M. Berger and C. Steel, *J. Am. Chem. Soc.*, **96**, 953 (1974).
- d. P. J. Wagner and R. A. Leavitt, *ibid*, **95**, 3669 (1973).
- e. G. Porter, S. K. Dogra, R. O. Loutfy, S. E. Sugamori and R. W. Yip, *JCS Faraday Trans I*, **69**, 1462 (1971).
5. G. Porter, R. W. Yip, J. M. Dunston, A. J. Cessner and S. E. Sugamori, *Trans Faraday Soc*, **67**, 3149 (1971).
6. J. Klein, V. P. Plazanet and G. Laustriat, *J. Chim. Phys. Physiochim. Biol.* **67**, 302 (1970).
7. J. B. Guttenplan and S. G. Cohen, *Tetrahedron Letters*, 2163 (1972).