Journal of Photochemistry, 12 (1980) 267 - 273

Preliminary Note

The quenching of biacetyl phosphorescence by alkenes: a dissection of rate effects on exciplex formation and exciplex decay for ketone triplet quenching

GUILFORD JONES, II, MAHALINGAM SANTHANAM and SHEAU-HWA CHIANG
Department of Chemistry, Boston University, Boston, Mass. 02215 (U.S.A.)
(Received July 18, 1979)

The quenching of ketone phosphorescence by alkenes has been the subject of a number of investigations [1]. The relationships between structure and reactivity for the interaction of ketone triplets and alkenes are important to the understanding of the well-known oxetane ring-forming Paterno–Buchi reaction [2] (Fig. 1). A number of ketone–alkene pairs appear to undergo cycloaddition by a triplet path (see for example ref. 3). Biacetyl has been shown to participate in the Paterno–Buchi cycloaddition in competition with a photochemical ene addition to alkenes [4] and a triplet mechanism including biradical intermediates (*e.g.* I) has been suggested [5]. We report results of the quenching of biacetyl triplets by alkenes including those important in photocycloaddition.

The quenching by a series of alkenes of the steady state biacetyl phosphorescence in nitrogen-purged or degassed benzene solutions at room temperature was analyzed using a Perkin–Elmer MPF44A instrument. Values of $k_q\tau_0$ from Stern–Volmer plots together with quenching constants k_q, calculated assuming a biacetyl triplet lifetime τ_0 of 0.46 ms [6] and including data from the literature, are shown in Table 1.

The pattern of quenching constants as a function of alkene structure was readily related to the electron donor properties of the alkenes. A reasonable fit of the data (Table 1) with alkene ionization potentials (IP) (correlation coefficient = 0.939) is shown in Fig. 2. The unusually effective quencher 2,5-dimethyl-2,4-hexadiene (DMH) was not included in the correlation since energy transfer from biacetyl (E_T = 56 kcal mol^{-1}) to DMH

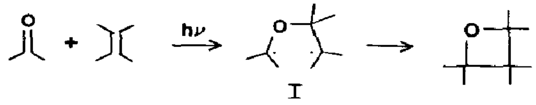

Fig. 1. The oxetane ring-forming Paterno–Buchi reaction.

TABLE 1

Stern–Volmer constants for the quenching of biacetyl phosphorescence by unsaturated compounds

Quencher	IP_v (eV)[a]	$k_q\tau_0$ (M^{-1})	k_q (M^{-1} s^{-1}) × 10^{-5}
2,5-Dimethyl-2,4-hexadiene	7.84	3.66×10^5	7960.0
Hexamethyldewarbenzene	7.90	1.04×10^3	22.6
Indole	7.92	–	129.0[b]
N-Methylpyrrole	7.95	1.25×10^3	27.2
trans-1-Phenylpropene	8.28	4.84×10^2	10.5
Dihydropyran	8.34	9.06×10^1	1.97
Tetramethylethylene	8.42	7.00×10^1	1.52
Indene	8.63	1.24×10^2	2.70
Cyclohexene	8.72	–	1.00[c]
Furan	8.89	3.15×10^1	0.68
Norbornene	8.95	–	0.24[d]
Ethyl vinyl ether	9.07	2.63×10^1	0.57
trans-2-Hexene	9.16	4.60	0.10
Methacrylonitrile	10.39	< 0.5	< 0.01

[a] Ionization potentials from the literature, derived mainly from photoelectron spectra.
[b] From ref. 7.
[c] From ref. 8.
[d] From ref. 9.

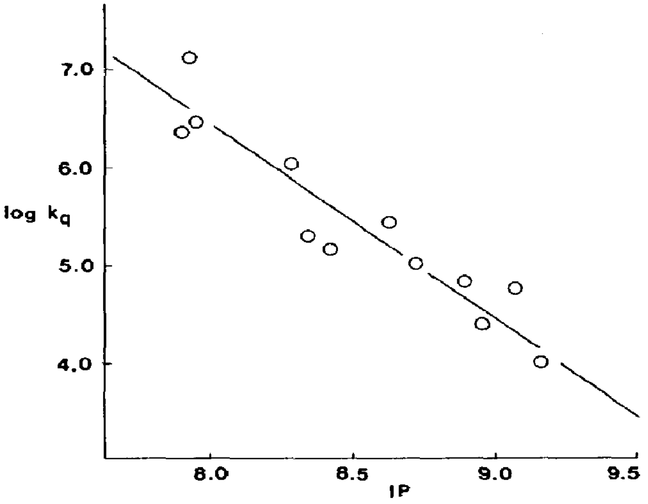

Fig. 2. The dependence of the biacetyl phosphorescence quenching constant on the ionization potentials (eV) of alkene quenchers (data from Table 1).

(E_T < 56 kcal mol^{-1} [10]) is probably important. It should be noted that energy transfer quenching of dicarbonyl triplets by conjugated dienes is well documented [6, 11].

TABLE 2

The quenching of emission from n,π^* carbonyl excited states by alkenes as a function of quencher ionization potential

System	*Solvent*	*IP dependence*[a]	*Reference*
Fluorescence quenching			
Acetone–alkenes	Hexane	— 1.28	12
Acetone–enol ethers	Acetonitrile	— 2.10	13
Biacetyl–alkenes	Acetonitrile	— 2.10	14
Biacetyl–enol ethers	Acetonitrile	— 2.70	14
Phosphorescence quenching			
Acetone–alkenes	Acetonitrile	— 1.66	1
Acetone–enol ethers	Acetonitrile	— 1.50	13
Benzophenone–enol ethers	Freon	— 1.65	13
Butyrophenone–alkenes	Benzene	— 1.09	15
Biacetyl–alkenes	Benzene	— 1.90	This work

[a] Slopes of plots of log k_q *vs.* IP of alkenes.

The dependence of the quenching constant on the alkene ionization potential is consistent with the behavior of other ketone triplets [1] and is reminiscent of relationships established for the quenching of alkanone and alkanal fluorescence. A summary of data (Table 2) shows the near uniform dependence of the emission quenching rate for n,π^* carbonyl excited states on the electron donor properties of alkenes. The slopes of IP plots ($\Delta \log k_q / \Delta \mathrm{IP}$) have an average value of -1.78 ± 0.38 eV^{-1}.

In studies of carbonyl emission quenching, apparent donor–acceptor interaction has usually been associated with the formation of excited complexes [1, 12 - 15]. Although exciplexes of simple ketones and alkenes have not been directly detected, in fluorescence quenching their intermediacy has been inferred from the temperature dependence of the quenching constants [12]. Deviant Stern–Volmer behavior has been associated with reversible formation of exciplexes in the quenching of glyoxal phosphorescence by alkenes in the gas phase [16].

For bimolecular decay of biacetyl triplets and alkenes, reversible exciplex formation and deactivation involve the steps

$$^3\text{Biacetyl} + \text{Alkene} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} {}^3\text{Exciplex} \xrightarrow{k_2} \text{Product} + \text{Biacetyl} + \text{Alkene}$$

The phosphorescence quenching constant for this simple kinetics scheme is given by

$$k_q = \frac{k_1 k_2}{k_{-1} + k_2}$$

and

$$k_q = K_1 k_2 \qquad k_{-1} \gg k_2 \qquad K_1 = k_1/k_{-1}$$

The dependence of the quenching rate on the alkene ionization potential follows from proportionalities associated with charge transfer within sensitizer–quencher encounter pairs [17].

$$\log k_q \propto \log K_1 \propto \Delta G_{ct} \propto E_{ox} \propto \mathrm{IP}$$

$$\Delta G_{ct} = E_{ox} - E_{red} - E_T - e^2/\epsilon r - T\Delta S \qquad (1)$$

where E_{ox} and E_{red} are standard redox potentials for alkenes and biacetyl in their electronic ground states, E_T is the biacetyl excitation energy and $e^2/\epsilon r$ is a coulombic term*.

Loutfy *et al.* [1] have used eqn. (1) in an extensive treatment of reversible exciplex kinetics for alkene quenching of ketone phosphorescence. The implication of this work is that, for a given ketone and a series of quenchers, $\log k_q \propto \log K_1$ is the important relation, whereas structural effects on k_2 are less important and are not related to the principal donor–acceptor interaction represented by K_1. (For acetone and donor alkenes a two-hundredfold range was calculated for K_1 as opposed to a twentyfold change in k_2 in the opposite direction [1].) We paid special attention to the change in the phosphorescence quenching constant for a series of ketones with a single alkene. The sample of data (Table 3), taken from other studies [1] and including our biacetyl results, shows that structural changes in the ketone lead to large variations in the quenching constants. It should be noted that the dependence is not uniformly associated with the redox driving force ($E_{red} + E_T$) for the ketones.

Since the exciplex formation constants are expected to be similar for different ketones and a single quencher (ΔG_{ct} values are similar, assuming common coulombic and entropy factors), the relative quenching rates may reflect changes in the exciplex decay rate. The makeup of k_2 is complex as it includes rate constants for product formation as well as parameters for unproductive decay to ketone and starting alkene. One factor that is likely to be important is the ketone excitation energy, *i.e.* the driving force for surmounting decay barriers, which is revealed by the general diminished

---

*The slopes of IP plots for carbonyl emission quenching are small relative to the values expected if full electron transfer from quencher to excited ketone is rate determining (maximum slope = $\Delta \log k_q/\Delta G_{ct} = 1/2.3\,RT = 17\ \mathrm{eV}^{-1}$, assuming that $\Delta G_1^{\ddagger}$ is a monotonic function of ΔG_{ct} [17]). For modest donor–acceptor interaction in quenching, the ΔG_{ct} function is best understood as an indicator of the mutual polarizability of excited states and quenchers, *i.e.* the mixing of locally excited and charge transfer configurations, rather than an association with outright electron transfer.

TABLE 3

Ketone triplet energies, reduction potentials and rate constants for the quenching of ketone phosphorescence by alkenes

Ketone	E_T (eV)	$-E_{red}$[a] (V)	$E_T + E_{red}$ (eV)	k_q (M^{-1} s^{-1}) × 10^{-6}		
				Enol ether	*Tetramethylethylene*	*Norbornene*
Acetone	3.38	2.31	1.07	340[b]	51	43
Butyrophenone	3.13	2.03 (2.01)	1.10 (1.12)		460	37
Benzophenone	2.94	1.84 (1.55)	1.10 (1.39)	1100[b]	895	40
Biacetyl	2.42	(1.28)	(1.22)	0.20[c]	0.15	0.024

[a] Polarographic half-wave reduction potentials (*vs.* Ag/AgCl, CH_3CN or, in parentheses, *vs.* SCE, DMF) [1, 18].

[b] 1-Ethoxy-2-methylpropene.

[c] Dihydropyran.

reactivity of biacetyl [6, 19]. If the sequence ^{3}ketone → ^{3}exciplex → ^{3}biradical is important* then biradical stability, which along with E_T determines the exothermicity of biradical formation, will be reflected in k_2.

For biradical formation the effectiveness of the presumed reactive center (carbonyl oxygen) in alkene attack may be decisive. The delocalized nature of the non-bonding orbitals of biacetyl [20] compared with those of monoketones matches the greatly reduced reactivity of the dicarbonyl triplet†. Other factors which do not involve biradical intermediates may be important in determining the rate of direct exciplex decay. These include rotational and other motion away from an exciplex geometry which affects spin–orbit coupling and the rate of intersystem crossing to the ground state [22].

Acknowledgments

We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the U.S. Office of Naval Research for support of M.S. as a postdoctoral associate and the U.S. Department of Energy for support of S.C. through a research assistantship.

1 R. O. Loutfy, S. K. Dogra and R. W. Yip, *Can. J. Chem.*, *57* (1979) 342.
2 D. R. Arnold, *Adv. Photochem.*, *6* (1968) 301.
3 L. A. Singer, R. E. Brown and G. A. Davis, *J. Am. Chem. Soc.*, *95* (1973) 8638.
N.C. Yang, M. Kimura and W. Eisenhardt, *J. Am. Chem. Soc.*, *95* (1973) 5058.
H. A. J. Carless, *J. Chem. Soc., Perkin Trans. II* (1974) 834.
N. J. Turro, J. C. Dalton, K. Dawes, G. Farrington, R. Hautala, D. Morton, M. Niemczyk and N. Schore, *Acc. Chem. Res.*, *5* (1972) 92.
4 H.-S. Ryang, K. Shima and H. Sakurai, *J. Org. Chem.*, *38* (1973) 2860.
5 H.-S. Ryang, K. Shima and H. Sakurai, *J. Am. Chem. Soc.*, *93* (1971) 5270.
6 N. J. Turro and R. Engel, *J. Am. Chem. Soc.*, *91* (1969) 7113.
7 E. Fujimori, *Mol. Photochem.*, *6* (1974) 91.
8 H. L. J. Backstrom and K. Sandros, *Acta Chem. Scand.*, *14* (1960) 48.
9 R. R. Sauers, P. C. Valenti and E. Tauss, *Tetrahedron Lett.*, (1975) 3129.
10 R. E. Kellogg and W. T. Simpson, *J. Am. Chem. Soc.*, *87* (1965) 4230.
11 A. W. Jackson and A. J. Yarwood, *Mol. Photochem.*, *8* (1977) 255.
F. B. Wampler and R. C. Oldenborg, *Int. J. Chem. Kinet.*, *10* (1978) 1225.

---

*In a future publication additional evidence that biradicals are formed on interaction of biacetyl triplets and alkenes will be presented. The evidence will include the observation of nearly complete loss of stereochemistry on photoaddition of biacetyl and 1,2-dimethoxyethene.

†For relatively "slow" reactions of ketone triplets and alkenes, a path of direct attack to give biradicals and not involving exciplexes is not excluded (although arguments can be made against this route [21]). The IP correlation for phosphorescence quenching would then be understood as the result of semipolar radical attack by electrophilic carbonyl triplets. Another complicating feature in slow triplet quenching is the intervention of hydrogen abstraction as a competitor to the pathway leading to cycloadducts. Hydrogen abstraction may be direct or may also involve an exciplex and have semipolar characteristics as well.

12 N. C. Yang, M. H. Hui, D. M. Shold, N. J. Turro, R. R. Hautala, K. Dawes and J. C. Dalton, *J. Am. Chem. Soc.*, *99* (1977) 3023.

13 N. E. Schore and N. J. Turro, *J. Am. Chem. Soc.*, *97* (1975) 2482.

14 B. M. Monroe, C.-G. Lee and N. J. Turro, *Mol. Photochem.*, *6* (1974) 271.

15 I. E. Kochevar and P. J. Wagner, *J. Am. Chem. Soc.*, *94* (1972) 7512.

16 J. T. Yardley, *J. Am. Chem. Soc.*, *94* (1972) 7283.

17 D. Rehm and A. Weller, *Isr. J. Chem.*, *8* (1970) 259.

18 T. Asano, K. Ohkata and T. Hanafusa, *Chem. Lett.*, (1974) 1149.

19 J. C. Scaiano, *J. Photochem.*, *2* (1973/74) 81.

20 E. Drent and J. Kommandeur, *Chem. Phys. Lett.*, *14* (1972) 321.

21 I. E. Kochevar and P. J. Wagner, *J. Am. Chem. Soc.*, *94* (1972) 3859.

22 N. D. Epiotis and S. Shaik, *J. Am. Chem. Soc.*, *100* (1978) 29.
N. J. Turro and V. Ramamurathy, *Mol. Photochem.*, *8* (1977) 239.