

ELECTRON TRANSFER CONTRIBUTIONS TO THE QUENCHING OF
AROMATIC KETONE PHOSPHORESCENCE BY ELECTRON-POOR OLEFINS

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Summary: The rate constant k_{ir} for quenching diaryl ketone triplet states by electron poor olefins in CCl_4 at room temperature decreases with decreasing reduction potential of the olefin. Unlike in previous cases, our data here fit the Weller equation, which predicts that $\ln k_{ir} \sim 1/RT$.

The quenching of both the fluorescence and phosphorescence of ketones by quenchers which act as good electron-donors or electron acceptors has been postulated to proceed via an exciplex intermediate.¹ These exciplexes are stabilized by charge transfer interactions, and it is often possible to correlate the electron-donor-acceptor properties of the substrates with their reactivity. In this paper we report the rate constants for quenching (k_{ir}) of the phosphorescence of benzophenone-4-methylcarboxylate (K^{*3}) by several chloroethylenes and by fumaronitrile. We show that k_{ir} can be correlated with the electron accepting properties of the olefins.

Values of k_{ir} for the quenching of K^{*3} by olefin was obtained by studying the phosphorescence decay of the excited state in varying concentration of quencher according to the Stern-Volmer expression, $(1/\tau) = 1/\tau_0 + k_{ir}[Q]$. This method has already been detailed elsewhere.² The rate constants for the photoreaction of K with the series of electron-poor olefins along with the half-wave reduction potentials of these olefins are listed in the table. Also included for comparison are the k_{ir} values for the photoreaction of triplet acetone and triplet butyrophenone reported by Loutfy³ and by Wagner,⁴ respectively.

Traditionally, values of k_{ir} are correlated with the free energy change ($\Delta G_{e.t.} = E_D^{ox} - E_A^{red} - e^2/\epsilon r - E^*$) for the transfer of an electron from one reactant to another, in this case from excited ketone to olefin. This analysis is based upon a treatment developed by Weller⁵ for bimolecular singlet state electron-transfer reactions where the reaction partners

were aromatic hydrocarbons. In his studies he found that $\ln k_{ir}$ values plotted against calculated ΔG_{et} values yielded two limits: when $\Delta G_{et} < -5$ kcal/mole, $\Delta \ln k_{ir} / \Delta \Delta G_{et} = 0$ and $k_{ir} = k_{diff}$. In the other limit for $\Delta G_{et} > 3$ kcal/mole, $\ln k_{ir}$ varied linearly with ΔG_{et} with a slope equal to $-1/RT$ (-38.2 eV^{-1}).

Table. Triplet Quenching Rate Constants

$k_{ir}^{25^\circ\text{C}}$ (ketone), $10^7 \text{M}^{-1} \text{s}^{-1}$				
Olefins	$-E_A^{\text{red}}$, V (I.P., eV) ^a	Acetone ^b	Butyrophenone ^c	K ^d
Fumaronitrile	0.8	650	580	621
Tetrachloroethylene	1.38 (9.34)	68.5	145	101
Trichloroethylene	1.64 (9.65)	42	42	5.0
1,1,-Dichloroethylene	1.90 (10.0)	-	-	0.38
trans-1,2-Dichloroethylene	1.75 (9.81)	18	40	0.80
cis-1,2-Dichloroethylene	1.77 (9.83)	17	16	0.18

a. Data taken from Ref. 3b; b. in CH_3CN ; c. in benzene; d. in CCl_4 ,
K is benzophenone-4- CO_2CH_3 . These rate constants are not very sensitive to solvent polarity, Ref. 6.

Previous studies of ketone fluorescence and phosphorescence quenching by both electron donors and by electron acceptors, gave plots of $\ln k_{ir}$ vs $\Delta G_{e.t.}$ with slopes in the range 2-6 eV^{-1} . Loutfy^{3b} has argued that although the dependence of $\ln k_{ir}$ upon ΔG_{et} indicates qualitatively that charge transfer intermediates are involved, a mechanism in which a full electron is transferred cannot be invoked. Instead he proposed that the slopes are equal to $-b^2/RT$, where b^2 was the fraction of an electron that is transferred. It was assumed that b^2 was constant for a single excited state ketone being quenched by a series of electron-donors or electron-acceptors, and values of $b^2 = 5-15\%$ were obtained. In particular, the photoreaction of triplet butyrophenone and triplet acetone with electron-poor olefins gave values of b^2 of 6% and 8% respectively.^{3b}

Other authors, particularly Wagner,⁷ have objected to this treatment. They take the point of view that the extent of electron transfer ought to depend upon electron demand. Good donors or good acceptors should experience a greater fraction of electron transfer than poor donors or poor acceptors.

The rate constants for the quenching of diaryl ketones triplet excited states by a series of electron-poor olefins have not been previously reported. Values of $\ln k_{ir}$ for the photo-reaction of K are plotted against E_A^{red} values of the olefins in the Figure. This plot shows as well the dependence of $\ln k_{ir}$ upon ΔG_{et} , since for one excited state ketone acting as an

electron donor to a series of olefins, $\Delta G_{et} = \text{constant} - E_A^{\text{red}}$ (olefin). Also included on this plot are the data for acetone and butyrophenone.

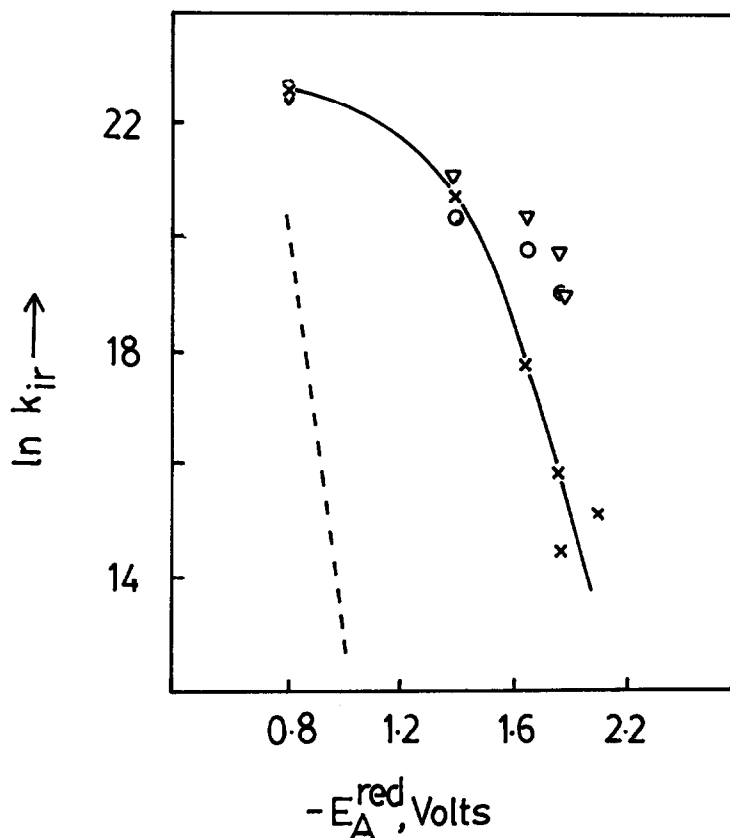


FIGURE: Dependence of $\ln k_{\text{ir}}$ upon E_A^{red} (olefin) for the photo-reaction of electron-poor olefins with K^{*3} (x), butyrophenone*³ (∇) and acetone*³ (o). The dashed line shows the slope predicted by the equation $\ln k_{\text{ir}} \sim 1/RT$.

We have obtained a larger range of rate constants for K than has been observed for acetone and butyrophenone.⁸ Our results show a non-linear dependence of $\ln k_{\text{ir}}$ upon E_A^{red} . The deviation from linearity for fumaronitrile is expected, since this reaction is nearly diffusion-controlled.⁵ The limiting slope can be estimated to be $\sim 20 \text{ eV}^{-1}$ from which $b^2 \sim 0.6$ can be calculated. In fact the uncertainty in the olefin reduction potentials are sufficiently large that a b^2 value of unity is consistent with our results. The sensitivity of k_{ir} to polar effects that we report here is much larger than any previously reported in ketone photochemistry.

ACKNOWLEDGMENTS

The authors thank NSERC Canada for their generous financial support. We found discussions with R.O. Loutfy and J.C. Scaiano very helpful. We also express our gratitude to Dr. Loutfy for measuring E_A^{red} and E_D^{ox} for K.

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8. Vertical triplet energy transfer as the quenching mechanism can be excluded by the observation that acetone [$E_T = 3.36$ eV, $E_D^{\text{ox}} = 2.59$ V]³ is not quenched more effectively by the chloroethylenes in the Table than is butyrophenone [$E_T = 3.13$ eV, $E_D^{\text{ox}} = 2.34$ V]³. E_D^{ox} for K was determined by Loutfy to be 2.60 V in CH₃CN using the methods he has previously reported.³ It has $E_T = 2.84$ eV.

(Received in USA 26 March 1982)