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ON THE INTERACTION OF EXCITED CARBONYL COMPOUNDS WITH GROUP V ORGANOMETALLICS.

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During the last few years considerable effort has been devoted to the study of the quenching of excited carbonyl compounds in processes involving charge-transfer interactions[2,3]. Reaction (1) shows a typical quenching mechanism,

$$A^* \quad + \quad Q \quad \rightleftharpoons [A,Q]^* \longrightarrow A \quad + \quad Q \quad \text{(or products)} \qquad (1)$$

where the intermediate [A,Q]* can involve variable degrees of charge transfer[3,4].

The Ph_3M series (where M=N,P,As,Sb,Bi) presents some interesting characteristics. All the compounds in this group have a very low, and almost identical ionization potential (IP_D), with the only exception being the value for Ph_3N which is somewhat smaller. We hoped to be able to determine which other interactions, in addition to charge-transfer could be of importance in determining the differences in reactivity. Our preliminary results for butyrophenone triplets (see Table)[5] were encouraging and suggested that heavy-atom effects could play an important role (note the large increase in rate constant for the last two members of the Ph_3M series).

In order to determine whether this behaviour was common to singlets, as well as triplets, we examined the quenching of fluorenone fluorescence in two different solvents using the lifetimes reported by Monroe and Groff[6,7]. The rate for Ph_3Sb is higher than for Ph_3As, but the value for Ph_3Bi is almost the same as for Ph_3Sb and still considerably lower than the rate of diffusion (compare with Ph_3N), suggesting that the increase in rate cannot be solely attributed to external heavy-atom effect. We propose that the lack of an increase in rate for Ph_3Bi should be attributed to a decrease in the availability of the lone electron pair in M. Structural studies in the group V organometallic show a steady decrease of the C-M-C angle along the series[8-10]. For antimony compounds it has been suggested that "...the lone pair must have appreciable p character."[9], while for Ph_3Bi "...there is virtually no hybridization of the 6s and 6p orbitals..."[10]

Rate Constant for the Interaction of Excited
Carbonyls with Group V Organometallics.

KETONE	Butyrophenone[a]	Benzophenone	Fluorenone	Fluorenone
STATE	Triplet	Triplet	Singlet	Singlet
SOLVENT	Benzene	Benzene	Benzene	DMF
Ph_3N	6.8×10^9	7.6×10^8[b]	1.25×10^{10}	6.9×10^9
Ph_3P	2.4×10^9	3.6×10^8[c]	4.5×10^9	1.9×10^9
Ph_3As	1.1×10^9	-	1.3×10^9	7.5×10^8
Ph_3Sb	3.6×10^9	-	3.7×10^9	2.1×10^9
Ph_3Bi	1.3×10^{10}	-	3.2×10^9	1.7×10^9
Ph_3PO	see text	-	[d]	$\leq 1.8 \times 10^7$
$(PhO)_3P$	-	-	2.1×10^8	$\leq 4 \times 10^7$
Ph_2NH	-	-	3.0×10^{10}	7.7×10^9

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[a] at 28°C; [b] R.F. Bartholomew, R.S. Davidson, P.F. Lambeth, J.F. McKellar and P.H. Turner, *J.C.S. Perkin II*, 577 (1972); [c] R.S. Davidson and P.F. Lambeth, *Chem. Commun.*, 1098 (1969), see also ref. 2; [d] not detected.

We note that the application of the log *k* *vs.* IP_D relationship should be limited to those systems where the donor centre remains unchanged, otherwise IP_D cannot be regarded as the only parameter which determines the changes in the kinetics of the process.

Additional support for the importance of the lone electron pair in determining the rates of quenching comes from the Ph_3P, $(PhO)_3P$, Ph_3PO series, where the rate constants decrease as the degree to which the "lone pair" is engaged in bonding increases. In the Ph_3PO-butyrophenone system we were not able to measure the rate constant accurately because of the interaction between Ph_3PO and the intermediate Type II biradical; however, the rate is at least 100 times smaller than for Ph_3P.

Solvent effects are not large; in fact, they can be explained on the basis of changes in the rates of diffusion[11]. This would suggest that charge separation in the exciplex is not very large (see also ref. 4).

Finally it should be pointed out that the large rate constant for the Ph_3Bi-butyropheone system (as compared with Ph_3Sb) could also reflect a change in mechanism for this particular pair. We note that this is the only substrate for which chemical-change is important[5].

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References and Notes

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