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CORRELATION BETWEEN THE n,π^* TRIPLET ENERGY OF SOME ACETOPHENONES AND THE CORRESPONDING ELECTROREDUCTION POTENTIALS

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Abstract—The half-wave reduction potentials, $E_{1/2}$'s, of ten acetophenone derivatives have been determined in acetonitrile. A linear free-energy relationship was obtained between $E_{1/2}$ and the n,π^* triplet energy. This correlation enabled an estimate to be made of the n,π^* triplet energy of those acetophenones with π,π^* lowest triplet.

The n $\rightarrow$ π^* and $\pi \rightarrow \pi^*$ triplet transition energies can be written as follows:[1]

$$^3E_{jk} = \epsilon_k - \epsilon_j - J_{jk}$$

where ϵ_k and ϵ_j represent the orbital energies for the highest occupied and lowest vacant molecular orbitals respectively and J_{jk} is coulomb integral over the MO's j and k. It is well known that the polarographic reduction and oxidation potentials of organic compounds are closely related to the molecular orbital energies; the half-wave reduction potential ($E_{1/2}^{red}$) and oxidation potential ($E_{1/2}^{oxid}$) are linearly related to the energy of the lowest vacant and highest occupied MO, respectively. Correlations have recently been established between $^3E_{n,\pi}$ and $E_{1/2}^{red}$ for some benzophenones, thiobenzophenones[2] and some aliphatic aldehydes and ketones[3] and between $^3E_{\pi,\pi^*}$ and $E_{1/2}^{red}$ for some α,β-unsaturated ketones.[4]

In this work, a linear relationship between the n,π^* triplet energies of a series of acetophenone derivatives and the corresponding $E_{1/2}$'s was also obtained, however it was found to differ in slope from that of the benzophenones series.[2]

Reductions were carried out in non-aqueous acetonitrile solutions containing 0·05 M tetraethylammonium perchlorate: the experimental procedure has been previously described.[2] The half-wave reduction potentials of the acetophenone derivatives obtained from the ac wave,[2] are shown in Table 1.

It was anticipated that the reduction potentials would correlate with the n,π^* triplet energy, provided that ϵ_k and J_{jk} are constant throughout the series. Indeed, substitution of a group into the aromatic ring of acetophenone would leave the energy of the n-orbital largely unaffected because this orbital is orthogonal to the π-system.[5] On the other hand, the resonance interaction or even the inductive effect of the substituent will cause a pronounced effect on both the π and π^* level.[5] Therefore, it is reasonable to predict that the reduction potentials will correlate with the energy of the n,π^* triplet transition. The present data is plotted in Fig 1. The regression coefficient for the straight line fitted to the data by least squares analysis is greater than 0·999 and the equation of the straight line is:

$$^3E_{n,\pi} = -0{\cdot}42\,E_{1/2} + 2{\cdot}3\,\text{eV} \qquad (2)$$

The above correlation was obtained for acetophenone derivatives **1** to **5** (Table 1). The pub-

Table 1. Electrochemical data and triplet energies of some acetophenones 4-X-$C_6H_4COCH_3$

No.	X	$-E_{1/2}^{red}$ (V)	$E_T(n,\pi^*)^a$ kcal/mole	$E_T(\pi,\pi^*)^a$ kcal/mole
1	H	2·09	73·6	
2	Cl	1·93	72·1	
3	CF_3	1·80	70·9	
4	CN	1·62	69·5	
5	Br	1·82	71·2	
6	NO_2	0·72	(60·2)[b]	
7	CH_3	2·20	(74·4)[b]	73·0
8	MeO	2·28	(75·4)[b]	71·7
9	OH	2·39	(76·6)[b]	71·3
10	3-MeO	2·10	(73·7)[b]	72·4

[a] Ref. 6.
[b] Predicted n,π^* triplet energy as calculated from Eq. 2.

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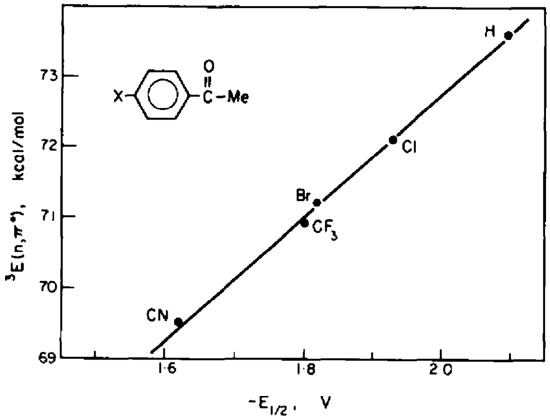

Fig 1. Plot of the half-wave reduction potentials of substituted acetophenones against the n,π^* triplet energies.

lished triplet transition energy data[6] for compounds **7–10** does not fit the above correlation. It should also be mentioned that Arnold[7] obtained a linear correlation between $^3E_{n,\pi^*}$ of some substituted acetophenones (**1–4**) and Hammett's σ constant, however, results for compounds **7** to **10** also did not fit his relation. This behaviour strongly indicates that the lowest transition for these compounds, **7–10**, is a $\pi \rightarrow \pi^*$ transition rather than a $n \rightarrow \pi^*$ transition.[8] Therefore, no correlation between the triplet energies for these compounds and $E_{1/2}$'s was obtained since substituents are expected to change the energy of both ϵ_k (in this case ϵ_π) and ϵ_j (ϵ_{π^*}).

The lowest triplet state of 4-bromoacetophenone **5** was assigned as a π,π^* state,[8] however from our correlation we believe that the lowest triplet state of **5** is n,π^* in nature and almost degenerate with the π,π^* triplet state.

From Eq. 2 the n,π^* triplet energy of those acetophenones with lowest $^3\pi,\pi^*$ can be calculated and the results are recorded in Table 1. The calculated n,π^* triplet energies for 4-hydroxy-, 4-methoxy- and 4-methylacetophenone (Table 1) are in good agreement with those obtained from the $S \rightarrow T_{n,\pi^*}$ absorption spectra of these compounds determined by the phosphorescence excitation method.[8,9]

Fig 1 has a slope of 0·42 which is higher than that for the benzophenone series, which indicates a greater sensitivity of the energy of the π^*-level of acetophenone to substituents.

The correlation obtained between $E_{1/2}$'s and $^3E_{n,\pi^*}$ of acetophenone derivatives could be utilized combined with the electrochemical data to predict the n,π^* triplet energy for those acetophenones whose $^3E_{n,\pi^*}$ is not available spectroscopically. The above relationship could also be used to determine the nature of the triplet transition as demonstrated here.

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