Electronic Spectra, Hyperconjugation, and the Baker–Nathan Effect.

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The spectra of diphenyl, acetophenone and its oxonium salt formed in concentrated sulphuric acid, aniline, the phenoxide ion and some of their 4-alkyl derivatives are determined. The varying effect of the alkyl groups on the *K*-bands shows that their electron-donating character increases in the normal inductive order Me $<$ Et $<$ Pr^i $<$ Bu^t and that the differences between the alkyl groups are enhanced with the increase of electron demand. The absence in electronic spectra of a hyperconjugative electron-release increasing in the order $Bu^t \longrightarrow$ Me is discussed.

It has been pointed out recently that the Baker–Nathan effect is encountered only in chemical equilibria and other changes in which bond contractions and bond stabilizations within one of the two entities involved play an important part, that in contrast it is not observed in physical properties such as dipole moments, ionization potentials and, anticipating the present investigation, electronic spectra which do not involve bond contractions, and that, in our view, it cannot be accounted for by the conception of hyperconjugation which moreover is not required for its interpretation (Burawoy and Spinner, *J.*, 1954, 3752).

The influence of substituents on light absorption is of considerable complexity, being dependent on both their position and the type of the electronic transition involved, *i.e.*, the type of absorption band under consideration [for their classification as *R*-, *K*-, and *B*(benzenoid)-bands, see Burawoy, *Ber.*, 1930, **63**, 3155; 1931, **64**, 464, 1635; 1932, **65**, 941; *J.*, 1939, 1177; *Discuss. Faraday Soc.*, 1950, **9**, 70]. Qualitatively, the *K*-bands of high intensity are best understood. They are due to transitions involving electron migrations (perturbations) along the (axis of) conjugated systems (I) (cf., *e.g.*, McMurry and Mulliken, *Proc. Nat. Acad. Sci.*, 1940, **26**, 312, and earlier papers; Calvin and Lewis, *Chem. Rev.*, 1939, **25**, 303). One important factor determining the position of a *K*-band is the polarity of such systems, *i.e.*, influences increasing their polarity (in the ground state) facilitate the electron migration and displace the *K*-band to longer wavelengths. It could be, therefore, expected that an investigation of the effect of terminal alkyl groups (I; A or B) of certain conjugated systems on the position of the corresponding *K*-bands would give information about the order of electron release by alkyl groups in the ground state (as well as in the excited state).

$$\text{(I)}\quad \underrightarrow{\mathrm{A\cdot[CH{:}CH]_n\cdot B}} \qquad \text{(II)}\quad \underrightarrow{p\text{-}\mathrm{R\cdot C_6H_4\cdot COMe}} \qquad \underrightarrow{p\text{-}\mathrm{R\cdot C_6H_4\cdot CMe{:}\overset{+}{O}H}}\quad \text{(III)}$$

The *K*-bands of the alkylbenzenes (at approximately 2000 Å) in heptane solution have been measured by Platt and Klevens (*Chem. Rev.*, 1947, **41**, 301; *J. Chem. Phys.*, 1948, **16**, 832). They appear, unfortunately, only as shoulders superposed on the slope of the bands of higher intensity (maxima near 1850 Å) probably due to Rydberg transitions (for interpretations of this band system and relevant literature, see Hammond, Price, Teegan, and Walsh, *Discuss. Faraday Soc.*, 1950, **9**, 53; Burawoy, *ibid.*, p. 78), and the positions of the true maxima are uncertain. We have, therefore, determined the spectra of diphenyl and 4-methyl- and 4-*tert.*-butyl-diphenyl in hexane and alcohol. The *K*-bands show a slight, but definite red-shift from the methyl to the *tert.*-butyl homologue.

Brown and Reagan (*J. Amer. Chem. Soc.*, 1947, **69**, 1033) have already observed that (in *iso*octane) the *K*-band of *p*-*tert.*-butylnitrobenzene lies at slightly longer wavelengths than that of its methyl homologue. We have now found that the *K*-bands of the four 4-alkylacetophenones (II) in hexane and those of their oxonium salts (III) in concentrated sulphuric acid behave similarly and, in particular, that the red-shifts increasing in the order Me $<$ Et $<$ Pr^i $<$ Bu^t are appreciably greater for the oxonium ions than for the ketones.

After completion of this investigation, Sweeney and Schubert (*ibid.*, 1954, **76**, 4625) reported a similar investigation of the *p*-alkylbenzoic acids, 4-alkylacetophenones, and *p*-alkylnitrobenzenes in alcohol and the oxonium salts of the ketones and nitro-compounds in sulphuric acid. Their data for the ketone oxonium ions are in very good agreement with ours; their values for the ketones and nitro-compounds, on the other hand, indicate no shift from the methyl to the *tert.*-butyl derivative, contrary to Brown and Reagan's and our observations, but those for the benzoic acids show again the normal red-shift in the order Me ⟶ Bu^t. Our original determinations were carried out with a Hilger E3 quartz spectograph fitted with a Spekker photometer. The plates were carefully analysed and, although the absolute differences may be subject to some experimental error, the direction and order of the displacements in each series is certain. After appearance of Sweeney and Schubert's note, we also examined the spectra of 4-methyl- and -*tert.*-butyl-acetophenone in hexane and alcohol and those of the diphenyls in alcohol with a Hilger Uvispek Photoelectric Spectrophotometer, originally not available, and confirmed the general trend. Our results are reproduced in Table 1 together with Brown and Reagan's data for the nitro-compounds.

The position of the *K*-bands of all substances discussed so far is determined by the facility of the electron migrations along the axis of the absorbing conjugated system, proceeding from the alkyl group into the benzene ring as indicated in (II) and (III). The results discussed clearly indicate that the polarity of the absorbing system (in the ground state) increases in the inductive order Me < Et < Pr^i < Bu^t and, what is most important, that the differences are greatest in the ions, in which the electron demand on the alkyl groups is greatest. Moreover, the results show that, in spite of the greater electron demand in the excited state as compared with the ground state, the relative stability of the excited states also increases in the order Me ⟶ Bu^t, and more so in the oxonium ions than in the ketones.

TABLE 1. *Maxima of K-bands of compounds* p-R·C_6H_4·X.

	R:	H		Me		Et		Pr^i		Bu	
X	Solvent	λ	10^{-3} ε	λ	10^{-3} ε	λ	10^{-3} ε	λ	10^{-3} ε	λ	10^{-3} ε
NO_2	*iso*Octane *	2520	8·6	2640	10·3	—	—	2650	10·4	2650	10·7
COMe	C_6H_{14}	2387	12·5	2466	17·5	2470	17·0	2478	17·0	2478	20·0
,,	,, †	—	—	2472	16·2	—	—	—	—	2480	19·5
,,	EtOH †	—	—	2516	14·5	—	—	—	—	2524	16·0
CMe:$\overset{+}{O}$H	H_2SO_4	2950	28·0	3113	30·0	3128	30·0	3150	32·0	3155	28·0
Ph	C_6H_{14}	2467	19·0	2513	19·1	—	—	—	—	2524	22·0
	EtOH †	—	—	2523	21·0	—	—	—	—	2534	21·0
NH_2	EtOH	2344	8·0	2355	10·0	—	—	—	—	2354	12·0
	,, †	—	—	2362	10·0	—	—	—	—	2361	10·0
O^-	0·1N-NaOH	2345	11·0	2359	9·5	—	—	—	—	2357	13·0
	,, †	—	—	2366	8·8	—	—	—	—	2364	11·5

* Brown and Reagan, *loc. cit.* † Determinations with Uvispek Photoelectric Spectrometer.

It should be noted, however, that the *K*-bands of the parent compounds are displaced appreciably to longer wavelengths by the introduction of a methyl group into the 4-position. This red-shift is only partly due to the increased polarity of the system (in the ground state). As will be fully discussed in a forthcoming publication, the greater polarizability of the Me–C electrons as compared with the H–C electrons, *i.e.*, the "extension" of the absorbing conjugated system, is another important factor facilitating the electron migration which is less important for substituents in the methyl group. In order to ensure that the electron-donating power of the alkyl groups (in the ground state) is the decisive factor for the absorption changes observed for the alkyl homologues, the *K*-bands of *p*-methylaniline and the *p*-methylphenoxide ion were compared with those of their *tert.*-butyl homologues (cf. Table 1). In these substances the alkyl groups are at the negative end of the absorbing conjugated system, and the electon displacement determining the position of the *K*-bands proceeds now into the alkyl group as indicated in (IV) and (V).

$$\text{(IV)}\ \underleftarrow{p\text{-R}\cdot C_6H_4\cdot NH_2} \qquad \underleftarrow{p\text{-R}\cdot C_6H_4\cdot O^-}\ \text{(V)}$$

This is supported by the observation that the introduction of a methyl group in the *p*-position is responsible for much smaller red-shifts of the *K*-bands than in the substances discussed above. The polarity of the absorbing system in the direction of the electron migration determining the position of the *K*-band will now be reduced. This would result in a hypsochromic shift which, however, is masked by a slightly greater red-shift due to the increased polarizability of the Me–C electrons.

No significant difference in the position of the *K*-bands of the methyl and butyl homologues is observed, but the latter, certainly, do not absorb at longer wavelengths. It appears that the expected small hypsochromic displacement due to the change of polarity is partly or completely compensated by a red-shift due to the greater polarizability of the electron system of the Bu^t–C group.

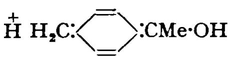
Matsen, Robertson, and Chuoke (*Chem. Rev.*, 1947, **41**, 273) have shown that the *B*-band systems of the alkylbenzene vapours are displaced to shorter wavelengths in the order Me ⟶ Bu^t and suggested that this was the spectroscopic analogue of the Baker–Nathan effect. Unfortunately, the effect of substituents on *B*-bands is complex and not well understood, but it may suffice to show that their positions in the spectra of monosubstituted benzenes cannot be taken as an indication of the polar effect of the substituents. This is illustrated in Table 2 by the maxima of the *B*-bands of the monohalogenobenzenes, phenol, and thiophenol which are compared with the corresponding *K*-bands. In contrast to the latter, the *B*-bands at least of iodobenzene and thiophenol are "anomalous." It appears that some unknown effect, which increases with the size of the substituent and may be of a steric nature but makes itself felt only in the electronic transition responsible for *B*-bands, causes displacements to shorter wavelengths. This matter requires further elucidation (cf. also Hammond, Price, Teegan, and Walsh, *loc. cit.*; Bowden, Braude, and Jones, *J.*, 1946, 948).

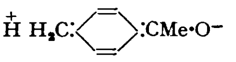
TABLE 2. *Maxima* (Å) *of B- and K-bands of compounds* $C_6H_5{\cdot}X$ *in alcohol.*

X	H *	F †	Cl †	Br †	I †	OH	SH
B-Band	2550	2540	2570	2610	2560	2730	2680
K-Band	2036	2040	2100	2100	2260	2105 *	2375

* Determinations in water by Doub and Vandenbelt, *J. Amer. Chem. Soc.*, 1947, **69**, 2714.
† Bowden and Braude, *J.*, 1952, 1068.

Discussion.—The hypothesis of an electromeric electron release by alkyl groups or of hyperconjugation was originally introduced to account for the Baker–Nathan effect (Baker and Nathan, *J.*, 1935, 519, 1940) and later applied to the interpretation of the shortening and strengthening of the C_{Me}–C bonds in substances such as propyne and of the effect of alkyl groups in electronic spectra (Pauling, Springall, and Palmer, *J. Amer. Chem. Soc.*, 1939, **61**, 927; Mulliken, *J. Chem. Phys.*, 1939, **7**, 339; Mulliken, Rieke, and Brown, *J. Amer. Chem. Soc.*, 1941, **63**, 41; cf. also Price, *Chem. Rev.*, 1947, **41**, 257; Walsh, *Ann. Rep.*, 1947, **44**, 32; for further references, see Baker, "Hyperconjugation," Oxford, 1952; Coulson, "Valence," Oxford, 1952). An extension of the conception of non-localized bonds, it postulates an electron release in the order Bu^t ⟶ Me which should be greatest when the electron demand on the alkyl group is strongest. It should be equally observed in chemical and spectroscopic changes. For instance, the hyperconjugated structure (VI) should contribute more strongly to the true structure of the oxonium ion of 4-methylacetophenone than the structure (VII) to that of the ketone itself, and the contribution of (VI) and (VII) should be still greater in the excited states of both.

(VI) 

 (VII)

The results of the present and Sweeney and Schubert's spectroscopic investigation exclude the presence of a hyperconjugative electron release of alkyl groups in the order Bu^t ⟶ Me in both the ground and the excited states of the examined substances. This lends additional experimental support to the conclusion that the valency conception of hyperconjugation does not account for the Baker–Nathan effect and the physical properties referred to above and, thus, its assumption is not required (Burawoy and Spinner, *loc. cit.*).

Shorter and Hinshelwood (*J.*, 1949, 4142), having found an indication of the Baker–Nathan effect in the rates of hydrolysis of the halides $R\cdot CMe_2Cl$, have, in this instance, suggested that a steric inhibition of solvation due to the increasing congestion round the charged carbon atom in the carbonium ions formed might make some contribution to this effect. Sweeney and Schubert (*loc. cit.*), in order to account for the striking contrast between the effect of alkyl groups in chemical and spectroscopic changes, suggested that this factor is of general importance for the Baker–Nathan effect. However, it is difficult to see how inhibition of solvation could make any important contribution to the Baker–Nathan effect observed, *e.g.*, in the ionization of 4-alkylbenzyl bromides or 3-alkyl-1 : 1-dimethylprop-2-ynyl chlorides, in which systems the alkyl groups are appreciably removed from the centre of the developing charge. Moreover, the Baker–Nathan effect is also observed in the dissociation constants of the *p*-alkylbenzoic acids (Baker, Dippy, and Page, *J.*, 1937, 1774), although steric inhibition of solvation (of the anion) would only reinforce the effect due to the normal inductive order of the alkyl group.

We have ascribed the Baker–Nathan effect to a steric resistance to bond contraction and stabilization, *e.g.*, of the bond R–C, as enforced by an increased positive charge at C in one of the two entities partaking in a chemical change, contraction and stabilization being reduced with the increasing size of the alkyl group (for details, see Burawoy and Spinner, *loc. cit.*; Burawoy, " Contribution a l'Étude de la Structure Moléculaire," Desoer, Liège, 1947—48, p. 73).

This interpretation, in contrast to that based on hyperconjugation, involves only inductive electron displacements and does not require that the decreasing stabilization of the linkage R–C in the order $Me{-}C \longrightarrow Bu^t{-}C$ is accompanied by a corresponding inversion of the order of the electron-donating powers of the alkyl groups or even of a reduction of their differences. In absence of any steric inhibition of bond contraction, an electron demand at the atom C would be responsible for an electron displacement increasing in the order $Me{-}C \longrightarrow Bu^t{-}C$, *i.e.*, the order of increasing polarizability of the systems. Our observations indicate that only the magnitude of these increases can be reduced by the steric inhibition of bond contraction.

In the past, interpretations of chemical and physical changes have been generally attempted in terms of polar effects and have proved, on the whole, to be successful in qualitative comparative discussions. However, equivalent changes of polarity of different linkages X–C involving different groups or atoms X (and possessing different bond energies) cannot be expected to be responsible for equal bond-energy changes, and it cannot be surprising that in isolated cases such as the Baker–Nathan effect (and possibly the similar behaviour of the halogen atoms in chemical changes, Burawoy, *op. cit.*, 1947—48) this relationship breaks down even qualitatively.

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