Acid-Base Properties of Electronically Excited States of Organic Molecules

J. F. IRELAND and P. A. H. WYATT

Department of Chemistry,
The University of St. Andrews,
Scotland

1. INTRODUCTION

This subject was initiated by Förster (1949), who took up Weber's earlier observation (Weber, 1931) that the fluorescence of 1-naphthylamine-4-sulphonate changes in wavelength at a markedly different pH from the absorption spectrum. Förster's work was developed by Weller and was reviewed by him in 1961, and by others later, viz., Vander Donckt (1970), Schulman and Winefordner (1970), and Schulman (1971a). A section on the subject also appears in new photochemical textbooks, among which we mention a clear exposition of its kinetic and chemical aspects by Parker (1968).

Weller's review (1961) is not confined to acid-base reactions but deals with the kinetics of excited state reactions in general. Vander Donckt (1970) covers developments of the acid-base section of the Weller field but pays more attention to physical organic aspects, such as applications of resonance theory to the interpretation of pK-shifts upon excitation and the application of linear free energy relationships. The reviews by Schulman and Winefordner (1970) and by Winefordner *et al.* (1971a) are directed towards possible analytical applications.

In the last few years more information on excited state pK-values has accumulated and the present review contains extensive reference tables of the experimental results in the literature available up to August 1974. We have confined our attention throughout to Brønsted acids and bases, though work on Lewis acid (donor-acceptor) systems continues (Weller, 1961; Birks, 1970; Ottolenghi, 1973) and may prove directly relevant to a deeper understanding of prototropic reactions, which must often be preceded by the formation of hydrogen-bonded complexes. Such interactions also play a role in solvent effects upon the absorption frequencies of acid and base molecules.

Where chemical processes such as protonation are concerned, it is the general rule that only the first excited singlet state (S_1) and the first excited triplet state (T_1) are involved. This is closely related to Kasha's rule for radiation emission (Kasha, 1950): fluorescence always occurs from the lowest excited singlet state and phosphorescence from the lowest triplet. Since experimental conditions are often arranged so that protonation is in competition with emission, i.e. so that their rates are similar, these rules are easily understood in terms of the much shorter time ($\sim 10^{-12}$ s) required for the S_1 state to be reached from the higher states produced immediately on absorption

than for the radiative and chemical changes to take place (10^{-8} s or longer). Exceptions do occur; it is well known that azulene fluoresces from the S_2 level, although the protonated forms of related compounds fluoresce from S_1 (Dhingra and Poole, 1968), and other cases of S_2 emission have been reported recently (Geldof *et al.*, 1969; Easterly *et al.*, 1970, 1973, 1974). Occasionally, simple chemical changes, e.g. electron transfer to a solvent, are believed to be rapid enough to involve higher states (Lesclaux and Joussot-Dubien, 1973).

The common pattern for all the compounds to be discussed can be summarized as follows. In the ground state the B and BH^+ species have all their electrons paired in the lowest molecular orbitals and are therefore in their lowest singlet states, S_0. Upon absorption of radiation, an electron is pictured as being promoted, without change of spin, to higher levels, S_1, S_2, etc., which are also usually vibrationally excited in a way that depends upon the relationship of the geometry of the higher electronic state to S_0, i.e. upon the Franck-Condon principle or the wave-function overlap between the states. Within about 10^{-12} s the molecule settles down (at room temperature) in the lowest vibrational level of the S_1 state by *internal conversion.* From S_1 it either emits *fluorescence* or, in the absence of any sufficiently rapid chemical changes, undergoes further internal con-
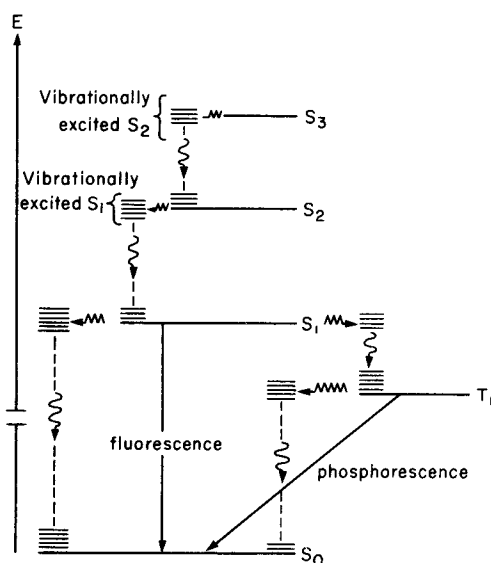

Figure 1. Radiative and radiationless decay processes in a polyatomic molecule (from Henry and Siebrand, 1973).

$S_2 \rightarrow S_1$, $S_3 \rightarrow S_2$, etc., because of the much larger electronic energy difference between S_1 and S_0). There is also usually time for the electron in the excited orbital to change its spin and thus to produce a vibrationally excited form of T_1 (or T_2, if low enough in energy) by *intersystem crossing*. After that, *phosphorescence* or radiationless conversion to the ground state (or further chemical reaction) may occur, but the rates of these spin-forbidden processes are generally much slower than the corresponding S_1 changes. For this reason triplet states figure much more prominently than excited singlets in photochemical discussions. These primary photophysical processes are summarized in Fig. 1, which is taken from the useful recent review of radiationless processes by Henry and Siebrand (1973).

That changes in acid and base strength upon excitation can be very important is evident upon considering the simple indicator equilibrium (1). For the base B to act as an indicator, it must absorb at a

$$BH^+ \rightleftharpoons B + H^+ \tag{1}$$

different frequency after protonation. Suppose that BH^+ absorbs at a higher frequency than B. If one then imagines a solution of pH equal to the ground state pK, so that $[BH^+] = [B]$, then upon excitation BH^+ will find itself at a higher energy level than excited B and will then (apart from relatively minor entropy effects) exhibit a strong tendency to change to B. In other words, it will become a stronger acid. If B absorbs at a higher frequency than BH^+, then B will become a stronger base on excitation.

At 300 nm, near which many molecules of interest absorb, the frequency is 10^{15} s^{-1}, corresponding to $\sim$400 kJ mole^{-1}. Thus a 30 nm shift in spectrum between B and BH^+ corresponds to $\sim$40 kJ mole^{-1} which makes a change of 7 units in pK. Since changes of 30 nm or more are common upon protonation, it is quite usual to find that the acid dissociation constant of a protonated compound changes by between 6 and 10 powers of ten after absorption of light. Our knowledge of such processes does not rely entirely upon absorption spectroscopy however; with the development of luminescence spectrophotometry and flash photolysis techniques it is now possible to study protonation equilibria directly in excited states.

The relationship suggested above between the frequency shift accompanying protonation (or any other chemical reaction) and the change in equilibrium constant upon excitation is formalized in the Förster cycle (Förster, 1950), illustrated in Fig. 2. Proceeding from
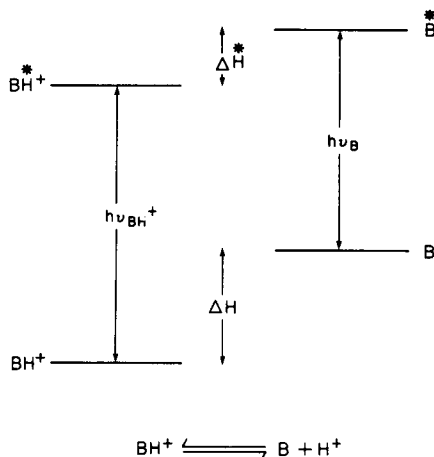
Figure 2. Förster's relationship of enthalpy changes to electronic transitions.

$$Lh\nu_{\mathrm{BH}^+} + \Delta H^* = Lh\nu_{\mathrm{B}} + \Delta H$$

i.e.

$$\Delta H^* - \Delta H = Lh(\nu_{\mathrm{B}} - \nu_{\mathrm{BH}^+}) \tag{2}$$

ground state BH^+ to excited B by two routes we are led to the equality (2), where ΔH^* and ΔH refer to the enthalpy changes in the excited and ground states respectively, and ν_{B} and ν_{BH^+} to the frequencies of the lowest absorption bands of B and BH^+; h is Planck's constant and L the Avogadro number.

If the solutions are dilute enough for ΔH to approximate to the standard value $\Delta H^\ominus$, or at least for the difference between ΔH^* and ΔH to approximate the difference $\Delta H^{*\ominus} - \Delta H^\ominus$, and if $\Delta S^\ominus$ does not change appreciably upon excitation so that $\Delta H^{*\ominus} - \Delta H^\ominus$ can be replaced by $\Delta G^{*\ominus} - \Delta G^\ominus$,

$$\Delta H^\ominus \sim \Delta G^\ominus = 2.303 \, RT \, \mathrm{p}K \tag{3}$$

If the temperature is 298°K, insertion of numerical values of constants gives (4).

$$\Delta \mathrm{p}K = 0{\cdot}00209(\bar{\nu}_{\mathrm{B}} - \bar{\nu}_{\mathrm{BH}^+})/\mathrm{cm}^{-1} \tag{4}$$

When, as above, the excited state is not specified, it is convenient to use the symbol $\mathrm{p}K^*$, but when a closer specification is required we can write $\mathrm{p}K(\mathrm{S}_1)$ or $\mathrm{p}K(\mathrm{T}_1)$, and $\Delta \mathrm{p}K$ will then stand for $\mathrm{p}K(\mathrm{S}_1) - \mathrm{p}K(\mathrm{S}_0)$ or $\mathrm{p}K(\mathrm{T}_1) - \mathrm{p}K(\mathrm{S}_0)$. Early results seemed to

version to S_0 by a radiationless process (at a rate which is slower than indicate that $pK(T_1)$ always lay between $pK(S_0)$ and $pK(S_1)$ and much closer to the former than to the latter, as in the classical case of 2-naphthol (Jackson and Porter, 1961); but as further results have accumulated it has become clear that $pK(T_1)$ may be nearer to $pK(S_1)$ than to $pK(S_0)$, as in anthroic acids (Vander Donckt and Porter, 1968a), and may even lie outside the $pK(S_1) - pK(S_0)$ range, as in xanthone and benzophenone (Ireland and Wyatt, 1972, 1973).

In view of the clear relationship between pK-changes and absorption spectra, a study of the influences of substituents and other consitutional changes upon such spectra has a very direct bearing upon the field of acid-base properties in excited states. For example, the $-OH$ and $-O^-$ groups function as different substituents at the 2-position in naphthalene. Any theory which accounts for their different effects upon the naphthalene transitions therefore automatically also explains the change in the naphthol-naphtholate equilibrium upon excitation. The search for linear free energy relationships in electronic spectra will therefore continue to impinge upon this field.

2. EXPERIMENTAL METHODS

Förster Cycle Determinations

Excited state pK-values are most easily accessible through the use of the Förster cycle which has been described in the introduction. To perform this calculation for a particular molecule it is necessary to know the ground state equilibrium constant for the reaction in question and to have some measure of the energy difference between the lowest vibrational level of the ground and the excited state in both the B and BH^+ forms. Thus to calculate $pK(S_1)$ we need the 0-0 energy of the S_0-S_1 transition and for $pK(T_1)$ that of the S_0-T_1 transition.

Methods of obtaining $pK(S_0)$-values are well documented (e.g., Albert and Sargent, 1962). Since the molecules of interest in excited state acid-base studies absorb at different wavelengths in the B and BH^+ forms, absorption spectroscopy is commonly used in the relevant ground-state pK-determination.

In proceeding to the excited state pK, it is not always easy to obtain a good value for the energy of the 0-0 transition except for

those cases in which the molecule shows vibrational fine structure in its absorption, fluorescence, or phosphorescence spectrum. Unfortunately, for most substituted aromatic compounds in solution, the absorption and emission spectra are characterized by broad, structureless long-wavelength bands, and the best that can be done is to use a maximum (or an obvious shoulder) of the longest wavelength feature. In either case, whether vibrational features are clear or the maximum of a broad band has to be used, the emission spectral data used in these calculations should always be obtained from the corrected spectra. The B and BH^+ forms will emit at different frequencies and the spectral correction factors can differ significantly. Methods of obtaining corrected emission spectra have been reviewed by Parker (1968) and by Argauer and White (1970).

In practice, handling S_0-T_1 transitions is often simpler (though less satisfactory), since absorption spectra are not normally available and the maxima of the B and BH^+ phosphorescence bands must then be used in the Förster cycle. However S_0-T_1 absorption spectra can sometimes be obtained, especially if perturbation methods can be used to enhance the singlet to triplet transition probability. For example, Grabowska and Pakula (1966) induced S_0-T_1 absorption in a series of nitrogen-containing heterocyclic compounds by the oxygen perturbation method of Evans (1957). Hence, for these compounds, by combination of absorption and phosphorescence spectral results, the 0-0 transitions could be located more accurately.

If the compound does not fluoresce, $pK(S_1)$-values can be calculated from the absorption maxima but they are then mainly of theoretical interest since the lifetime of the S_1 state is likely to be too short to allow the protolytic reaction ever to reach equilibrium. For compounds which fluoresce there are three approaches to obtaining a 0-0 energy approximation: (a) the use of absorption maxima, (b) the use of fluorescence maxima, and (c) the averaging of the absorption and fluorescence maxima of each form (Weller, 1952; Wehry and Rogers, 1965a). There has been much discussion as to which of these is the "best" method of obtaining the energy values needed for the Förster cycle, but in any case the sensitivity of the calculated energy to small errors in the location of the 0-0 band can be appreciated when it is recalled that, at 300 nm, an error of 4 nm corresponds to 1 unit of pK. The effects of solvation on 0-0 energies are further discussed in Section 4. In practice it is sometimes possible to make use of a special characteristic of the acid or base form of a particular compound and even to estimate the 0-0

transition energy differently for the two species. For example, in the case of several benzophenones (Ireland and Wyatt, 1973) the S_0-S_1 absorption of the base form in aqueous solution is obscured by the more intense S_0-S_2 transition but, since the phosphorescence excitation spectrum shows the vibrational spacing of the first transition, it is not difficult to get a good 0–0 value for the B form. On the other hand, the protonated forms of the benzophenones have broad, intense, long-wavelength absorption bands, but because they fluoresce, unlike the B forms, a good estimate of the 0–0 energy can be obtained by the averaging technique.

It is clear that the Förster cycle will only give precise pK^*-values in special cases, but it will at least indicate the direction of the pK-shift and in many cases will give a good approximation to the magnitude of the change. (When ΔpK is small, even the direction of the change may occasionally be incorrect, e.g. Ballard and Edwards, 1964a; Winefordner *et al.*, 1971b).

Fluorescence Titrations

The changes in molecular fluorescence with acidity give information about the protolytic behaviour of the excited singlet state of a compound. A p$K(S_1)$-value calculated from the Förster cycle gives an indication of the acidity range in which a fluorescence change is expected, but, since no account is taken of the relevant rates of the particular processes involved, the Förster cycle does not indicate whether or not proton transfer in the excited state is kinetically feasible. Improved instrumentation has made fluorescence techniques more available and extended the range of compounds accessible to the method because of improved sensitivity. The techniques of fluorescence spectroscopy are well known (Udenfriend, 1962; Parker, 1968; Argauer and White, 1970). To investigate the excited state behaviour of a particular compound the fluorescence intensity of the B and BH^+ forms (or that of B or BH^+ if only one of these fluoresces) is recorded at various values on the pH or other acidity scale (e.g. H_0).

If the fluorescence spectra of the acid base pair overlap, then the measured fluorescence intensities of BH^+ ($\mathscr{I}$) and B ($\mathscr{I}'$) must be corrected for the intensity component due to the other form. The true fluorescence intensities (ϕ and ϕ') are related to the measured intensities according to the equations:

$$\mathscr{I} = \phi + k'\phi' \tag{5}$$

$$\mathscr{I}' = \phi' + k\phi \tag{6}$$

where k and k' are the overlap ratios of the BH^+ and B forms respectively. To obtain the overlap ratios, measurements are made on solutions containing only one species in the excited state. Thus k is obtained from solutions showing only the characteristic fluorescence of the protonated form and is the ratio of the fluorescence intensity of BH^+ (measured at the analytical wavelength for B) to the intensity at the wavelength where BH^+ emission is measured. Similarly k' is obtained from measurements in a solution having B as the only fluorescent species. Rearranging eqns (5) and (6) we can obtain the true fluorescence intensities in terms of $\mathscr{I}, \mathscr{I}'$, k and k':

$$\phi = \frac{\mathscr{I} - k'\mathscr{I}'}{1 - kk'} \tag{7}$$

$$\phi' = \frac{\mathscr{I}' - k\mathscr{I}}{1 - kk'}. \tag{8}$$

In cases uncomplicated by quenching effects ϕ_0 and ϕ_0' values can be taken as the limiting value of the true fluorescence intensities at 2 or 3 pH units away from the half way point of the fluorescence change. The relative intensities (ϕ/ϕ_0 and ϕ'/ϕ_0') in the intermediate region can then be plotted against acidity. Figure 3 gives a plot of this type for the cation and zwitterion of 3-hydroxyquinoline
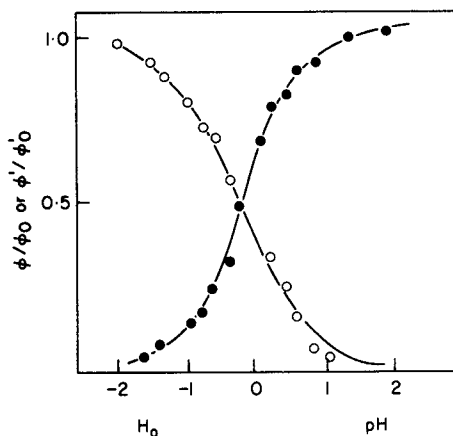

Figure 3. Acid dependence of 3-hydroxyquinoline fluorescence intensity: cation (○); zwitterion (●) (Haylock et al., 1963).

(Haylock *et al.*, 1963). Where complications due to non-equilibrium or quenching effects complicate the curve of one form so that ϕ_0 or ϕ_0' is not directly measurable (see e.g. Fig. 4), one may be determined from the other via the relationship (9).

$$\phi/\phi_0 + \phi'/\phi_0' = 1 \tag{9}$$

The inflection point of the fluorescence intensity curves against acidity gives a first approximation to the $pK(S_1)$-value but this involves the assumption that the protolytic equilibrium is established within the lifetime of the S_1 state and that the fluorescence lifetimes of B and BH^+ are equal. These assumptions are less likely to hold when only one form is fluorescent and Lasser and Feitelson (1973)
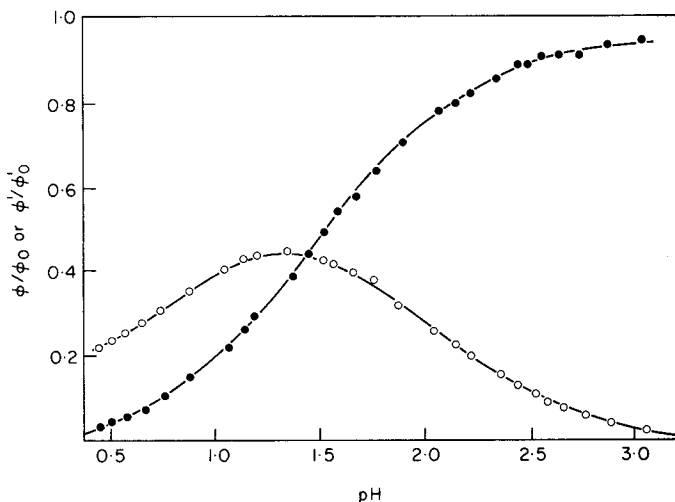

Figure 4. Acid dependence of 1-naphthamide fluorescence intensity: protonated form (○); unprotonated form (●) (Watkins, 1972b).

have concluded that fluorescence against pH curves do not give good $pK(S_1)$-values in such cases.

It can be shown (see Section 3) that for excited state equilibrium to be attained the relationships (10) hold, where τ_0' and τ_0 are the

$$\frac{1}{\tau_0'} \ll k_2[H^+] \quad \text{or} \quad \frac{1}{\tau_0} \ll k_1 \tag{10}$$

fluorescence lifetimes of B and BH^+ respectively, k_1 is the rate of dissociation of BH^+ and k_2 is the rate constant for protonation. It is not surprising that the system reaches equilibrium when the rate of fluorescence decay is considerably less than the protolytic rate constants. In these cases it is easily shown that eqn (11) holds, where

$$pH = pK(S_1) - \log \tau_0/\tau_0' \tag{11}$$

pH is the acidity at which the relative intensity curves show an inflection. To obtain corrected $pK(S_1)$-values we must therefore have a measure of excited state lifetimes.

Triplet-Triplet Absorption Titrations

This method for obtaining $pK(T_1)$-values was introduced by Jackson and Porter (1961). It is even more time-consuming compared to the Förster cycle than the fluorescence titration method and relatively few direct determinations have been made of $pK(T_1)$. The experimental techniques have recently been described by Chibisov (1970) and Labhart and Heinzelmann (1973). Developments in instrumentation, including the introduction of laser excitation, have been reviewed by Porter and West (1973).

For this technique to be applicable, one or both forms of an acid-base pair must show a T—T absorption. If, as in the case of xanthone (see Fig. 5), T—T absorption spectra are obtained from both forms, the observed optical densities must be corrected for any overlap in a manner analogous to that used for fluorescence inten-
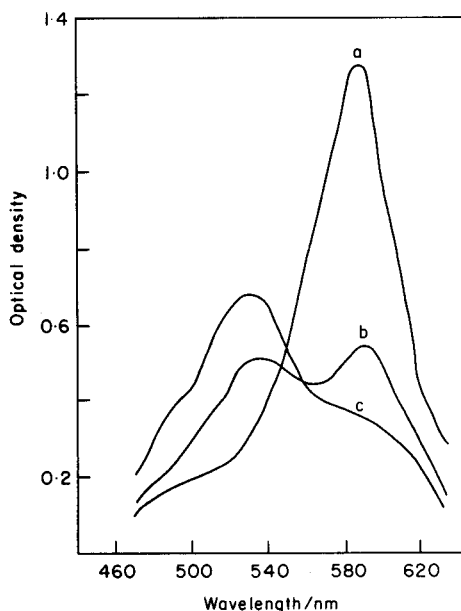

Figure 5. Triplet-triplet absorption of xanthone at three pH values: (a) pH = 7·0, (b) pH = 2·8, (c) pH = 2·1 (Ireland and Wyatt, 1972).

sities. From plots of the relative optical densities against pH, $pK(T_1)$-values can be obtained. For example, from Fig. 6 a value of 3.0 is obtained for $pK(T_1)$ for xanthone. The subsequent decrease in optical density of the BH^+ triplet around pH 1 as the acidity is increased, is caused by a protolytic reaction in the S_1 state. The BH^+ singlet form is a more efficient fluorescer than the B form, whence intersystem crossing is diminished and the BH^+ triplet state is not produced in such a high concentration as at lower acidities. This gives
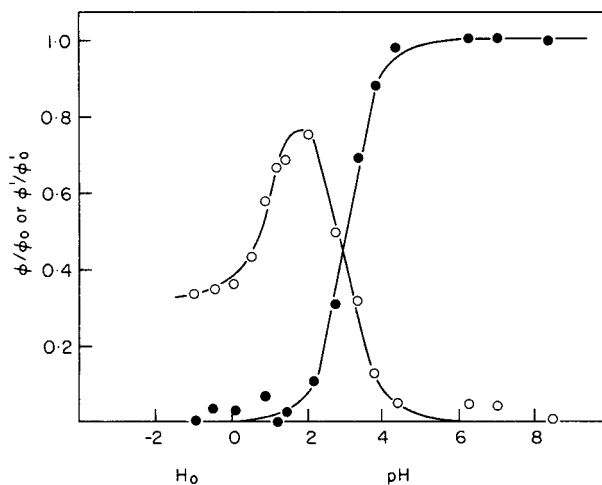

Figure 6. Relative optical densities of triplet-triplet absorption of protonated and unprotonated xanthone as a function of acidity: $\bigcirc$, ϕ/ϕ_0 at 530 nm (protonated form); $\bullet$, ϕ'/ϕ'_0 at 595 nm (unprotonated form) (Ireland and Wyatt, 1972).

confirmation of the $pK(S_1)$-value obtained by fluorescence titration, subject however to the same lifetime and equilibrium qualifications.

Owing to the longer lifetime of the triplet state it is expected that the protolytic reaction will usually reach equilibrium within the lifetime of the state. Unlike the fluorescence titration method for $pK(S_1)$ described above, the triplet-triplet absorption technique leads directly to $pK(T_1)$ without the necessity for a knowledge of lifetimes. Phosphorescence "titration" studies, on the other hand, will involve the lifetime term $\log \tau_0/\tau'_0$ just as for fluorescence.

The use of laser flash photolysis has extended this type of work to shorter-lived species and has enabled the initial triplet concentration to be monitored against pH (e.g. Rayner and Wyatt, 1974). There is a drawback at present in that the molecule under examination must absorb at a frequency dictated by the laser, but this restriction will probably become less severe as tunable lasers are developed.

One common complication in flash photolysis studies is the production from the excited state of radicals which may be confused with or inhibit observation of the triplet state. The radical species, which usually has a longer lifetime than that of the triplet state, may be identified by separate experiments (Jackson and Porter, 1961); but such species may themselves show interesting acid base properties (e.g. Lindqvist, 1960; Lindqvist and Kasche, 1965; Simic and Hoffman, 1972; Neta, 1975). Their optical density contributions may therefore change with acidity in the range studied.

Lifetime Measurements

Two techniques, phase and pulse fluorometry, are used for the direct measurement of fluorescence decay rates, and their principles are described by Birks and Munro (1967), Parker (1968), and Birks (1970). The photon sampling method has proved useful and versatile. This is an iterative technique in which single photons are counted as a function of the time at which they appear after excitation and a complete decay curve is built up. (For recent references see e.g. Zimmerman *et al.*, 1973, 1974). Wider use of the photon sampling technique will increase the precision of lifetimes obtained and extend the range of compounds studied to those with shorter lifetimes or very low fluorescence yields.

If no direct measurement of the fluorescence lifetime is available the relations between the radiative lifetime and the fluorescence and absorption spectra can be used in conjunction with the quantum yield to obtain an indication of the fluorescence lifetime. Birks and Munro (1967) have reviewed the methods of calculating the radiative lifetime. In general these methods are limited to specific groups of compounds. For example, Favaro *et al.* (1973) applied Stickler and Berg's (1962) formula to the spectral data obtained from an excited state acid-base study of some styrylpyridines and found a lack of quantitative agreement between the measured and calculated lifetimes.

Indirect Methods

Although fluorescence and T–T absorption titration methods are the most commonly used techniques for obtaining direct experimental evidence of $pK(S_1)$ and $pK(T_1)$, other less direct approaches

have been tried. Rosebrook and Brandt (1966) measured the potential between one illuminated electrode and one dark electrode in a solution of a base of interest. Changes in the "photopotential" with pH were related to the pK-value of the excited singlet state. The results obtained for naphthylamines and 3-hydroxypyridine were in agreement with those from fluorescence titration and Förster Cycle calculation. This method does not appear to have been extended, perhaps because of a limitation in the types of compound to which it may be applied.

Avigal *et al.* (1969) investigated the quenching effects of a series of carboxylate ions upon the fluorescence of substituted phenols. Rate constants for the quenching process, obtained from Stern-Volmer plots, satisfied the Brønsted general base catalysis law and extrapolation to the base strength of water then leads to an estimate of the rate of reaction between ROH* and H_2O. Assuming the reverse reaction to have a rate constant of 5×10^{10} dm^3 mole^{-1} s^{-1}, they were able to calculate values of $pK(S_1)$. This does not seem to be very different in principle from the method used by Weller (1957a) to determine $pK(S_1)$ for acridine. Since acridine is not protonated rapidly enough by H_3O^+ in the required region of pH, he determined the forward and reverse rate constants for protonation with a different acid, NH_4^+, and used the pK-value of NH_4^+ to obtain the $pK(S_1)$ of acridine in the H_3O^+–H_2O system.

The reactivity of the triplet state in photoreduction reactions was used by Nakamaru *et al.* (1969) to investigate the triplet state basicity of acridine. It should be possible to extend this method to any compounds in which an excited state reaction is affected by protonation.

3. KINETICS AND EQUILIBRIA OF
EXCITED STATE PROTONATION REACTIONS

In the earlier work (Förster, 1951; Weller, 1952) when the principal experimental information involved fluorescence intensities, the most useful algebraic expressions were those relating relative quantum yields of the conjugate acid base pair to the solution acidity. In favourable cases such expressions were used to obtain rate constants for the forward and reverse reactions, and hence equilibrium constants, though it was always necessary to make allowance

for the different lifetimes of the excited states of the species. With the development of laser flash and photon sampling techniques however, much greater possibilities have been opened up for the direct measurement and use of excited state lifetimes, and the equations derived for the rates of decay of luminescence or transient absorption intensities will therefore find increasing application.

The groundwork for the solution of the types of problem encountered was laid by Förster (1951) and Weller (1952, 1954, 1957a, 1957b, 1958a, 1958c, 1961) and some examples will now be given to illustrate their method of approach.

Singlet Decay

To simplify the initial presentation, very rapid local effects, sometimes encountered during the approach to the steady state, will be omitted. Further, only the simplest proton transfer reaction will be considered, along with allowances for quenching, emission and intersystem crossing. Such other possibilities as solvated electron formation or the secondary formation of radicals by hydrogen abstraction etc. will be ignored initially. The two principal types of derivations can then be illustrated directly in terms of the singlet decay scheme, which represents the processes which occur after a molecule absorbs light and reaches the first excited singlet state. The protolytic reaction, radiation transition, and fluorescence by the two excited species are all allowed for in (12). The concentrations of

$$
\begin{array}{ccc}
BH^+(S_1) & \xrightarrow[\ k_2[H^+]=k'_2\ ]{k_1} & B(S_1)+H^+ \\
k_q \swarrow \quad k_f \downarrow \quad \searrow k_T & & k'_T \swarrow \quad k'_f \downarrow \quad \searrow k'_q \qquad (12)\\
BH^+(S_0) \quad BH^+(S_0) \quad BH^+(T_1) & & B(T_1) \quad B(S_0) \quad B(S_0) \\
+h\nu & & +h\nu'
\end{array}
$$
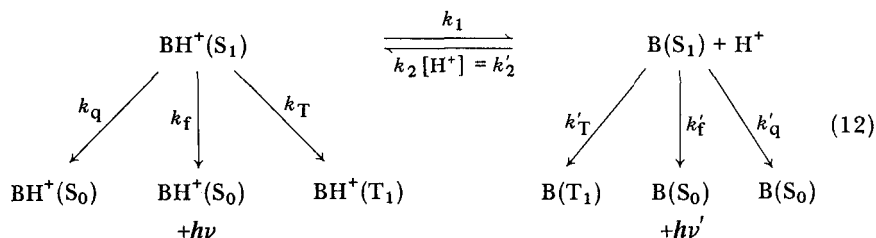
$BH^+(S_1)$ and $B(S_1)$, the protonated and unprotonated base species in the S_1 state, will be represented by x and y respectively, and the rate constant suffixes denote transitions to the ground state by solvent and other quenching (q), and by fluorescence (f), or transitions by intersystem crossing to the triplet state (T). Primed constants refer to the base species $B(S_1)$ and unprimed to the conjugate acid $BH^+(S_1)$. In the protonation equilibrium the rate

constant for the dissociation of $BH^+(S_1)$ is denoted by k_1 and the recombination rate is characterized by the effective first-order constant $k_2[H^+]$, which is contracted to k_2' for convenience ($[H^+]$ being constant in a given solution).

The rates of change of the $BH^+(S_1)$ and $B(S_1)$ concentrations can now be represented by the relations (13) and (14), where $a = k_1 + k_f$

$$\frac{dx}{dt} + ax = k_2'y \tag{13}$$

$$\frac{dy}{dt} + a'y = k_1x \tag{14}$$

$+ k_q + k_T$ and $a' = k_2' + k_f' + k_q' + k_T'$. These equations can sometimes be used directly on experimental results, as shown by Loken *et al.* (1972), who derived rate constants in this way which agreed well with those from the integrated solutions (15) and (16) (for which see also Weller, 1958a; Birks, 1970; Ofran and Feitelson, 1973; Rayner and Wyatt, 1974):

$$x = \frac{1}{2\sqrt{m}} \{[(\sqrt{m} + a - a')x_0 - 2k_2'y_0]e^{-\alpha t}$$

$$+ [(\sqrt{m} - a + a')x_0 + 2k_2'y_0]e^{-\beta t}\} \tag{15}$$

$$y = \frac{1}{2\sqrt{m}} \{[(\sqrt{m} - a + a')y_0 - 2k_1x_0]e^{-\alpha t}$$

$$+ [(\sqrt{m} + a - a')y_0 + 2k_1x_0]e^{-\beta t}\} \tag{16}$$

where

$$m = (a - a')^2 + 4k_1k_2'$$

$$\alpha = (a + a' + \sqrt{m})/2$$

$$\beta = (a + a' - \sqrt{m})/2$$

and x_0 and y_0 are the values of x and y at $t = 0$.

Clearly, in cases in which only BH^+ or B is excited (and no instantaneous conversion takes place before the steady state is set up), (15) and (16) are considerably simplified by setting $x_0 = 0$ or $y_0 = 0$. In specific cases the use of justifiable simplifications about the magnitudes of the components of a and a' can simplify the expressions still further. For example, if $y_0 = 0$ and the pH is high enough for k_2' to be very small compared with all the other rate

constants in a and a', (15) and (16) become (17) and (18), where $\tau =$

$$x = x_0\, e^{-t/\tau} \tag{17}$$

$$y = [k_1 x_0/(a - a')]\,(e^{-t/\tau'} - e^{-t/\tau}), \tag{18}$$

$1/(k_1 + k_f + k_q + k_T)$ is the lifetime of $BH^+(S_1)$ at e.g. neutral pH [as distinct from its lifetime $(k_f + k_q + k_T)^{-1}$ at low enough pH for only $BH^+(S_1)$ to be present] and $\tau' = 1/(k'_f + k'_q + k'_T)$ is the lifetime of B at high pH. Equations (17) and (18) were used, for example, by Loken *et al.* (1972) and Ofran and Feitelson (1973) in their studies of 2-naphthol lifetimes. The form initially excited dies away exponentially from x_0, while the other form grows from zero at a rate which initially depends only on $k_1 x_0$ (since for small values of t (18) reduces to $y = k_1 x_0 t$) and then passes through a maximum, just as would be expected (Fig. 7).

For molecules of interest, the excitation pulse and the instrumental response time will often be comparable to the lifetimes being measured and deconvolution methods will become necessary, so that
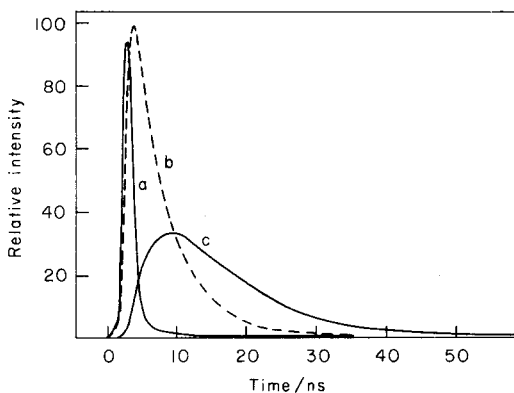

Figure 7. 2-Naphthol fluorescence decay curves at pH = 3·43: (a) flash profile; (b) 2-naphthol fluorescence intensity at 360 nm; (c) 2-naphtholate fluorescence intensity at 450 nm (× 2·5 relative to (b)) (from Loken *et al.*, 1972).

(17) and (18) are not immediately applicable to the experimental results as they stand (see e.g. Knight and Selinger, 1971; Demas and Adamson, 1971; Zimmerman *et al.*, 1974). While the general form of the time dependence is quite recognizable in the 2-naphthol study mentioned above (Fig. 7), new features can, however, emerge when the curve-fitting is carried out carefully. Ofran and Feitelson (1973)

found that they could only fit their curve properly if they assumed that some of the naphtholate form was produced in the S_1 state so rapidly after excitation as to justify introducing a y_0 value different from zero. This point will be referred to later, but at this stage we may note that effects of this kind can certainly affect the interpretation of the curves as late as 20 or 30 ns after excitation. The most important outcome is, however, that a study of the changes in τ and τ' with changes in experimental conditions can lead to the determination of k_1 and k_2 and hence directly to k_1/k_2, the excited state equilibrium constant.

The pH-Dependence of Fluorescence Intensities

When only fluorescence intensities in steady state conditions have to be handled, some of the mathematical manipulation for the complete solution of (13) and (14) can be by-passed. Weller (1952) then focuses attention upon the probability, ρ, that a molecule will still be in the excited state at time t after excitation. If the molecule concerned is the initial absorber of the exciting radiation, $\rho_0 = 1$ at $t = 0$: in this case ρ at some other time t will be equivalent to x/x_0 in the above treatment. In these terms (13) and (14) become (19) and (20), while the fluorescence quantum yields ϕ and ϕ' are given by

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} + a\rho = k'_2\rho' \tag{19}$$

$$\frac{\mathrm{d}\rho'}{\mathrm{d}t} + a'\rho' = k_1\rho \tag{20}$$

(21) and (22). Since these yields are $\phi_0 = k_f/(k_f + k_q + k_T) = k_f\tau_0$

$$\phi = \int_0^\infty k_f\rho \, \mathrm{d}t \tag{21}$$

$$\phi' = \int_0^\infty k'_f\rho' \, \mathrm{d}t \tag{22}$$

and $\phi'_0 = k'_f/(k'_f + k'_q + k'_T) = k'_f\tau'_0$ respectively when only one species is present in the excited state, the quantum yields relative to ϕ_0 and ϕ'_0 are given by (23) and (24).

$$\phi/\phi_0 = (1/\tau_0) \int_0^\infty \rho \, \mathrm{d}t \tag{23}$$

$$\phi'/\phi'_0 = (1/\tau'_0) \int_0^\infty \rho' \, dt \tag{24}$$

These two equations then allow substitution of $\int_0^\infty \rho \, dt$ and $\int_0^\infty \rho' dt$ in the integrated forms of (19) and (20) by $\tau_0 \phi/\phi_0$ and $\tau'_0 \phi'/\phi'_0$ and, with $\int_0^\infty d\rho = \rho_\infty - \rho_0 = -\rho_0$ and $\int_0^\infty d\rho' = -\rho'_0$, yield finally eqns (25)

$$\frac{\phi}{\phi_0} = \frac{a'\rho_0 + k'_2\rho'_0}{\tau_0(aa' - k_1k'_2)} = \frac{\rho_0 + k'_2\tau'_0(\rho_0 + \rho'_0)}{1 + k_1\tau_0 + k'_2\tau'_0} \tag{25}$$

$$\frac{\phi'}{\phi'_0} = \frac{k_1\rho_0 + a\rho'_0}{\tau_0(aa' - k_1k'_2)} = \frac{k_1\tau_0(\rho_0 + \rho'_0) + \rho'_0}{1 + k_1\tau_0 + k'_2\tau'_0} \tag{26}$$

and (26). Two special cases will illustrate the application of these equations.

Case I: the compound is in the BH^+ form in the ground state and this is the only form excited. Then $\rho_0 = 1$, $\rho'_0 = 0$, and (25) and (26) reduce to the equations used originally by Weller (1952) to describe the variation with pH of the ultraviolet and blue fluorescence intensities of 2-naphthol, shown in Fig. 8 (see also Parker, 1968).
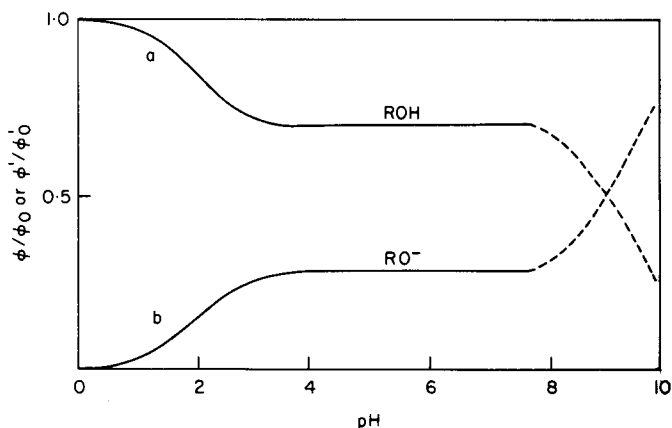
Figure 8. Acid dependence of 2-naphthol fluorescence: (a) 2-naphthol; (b) 2-naphtholate (Weller 1958a).

At low pH any excited naphtholate ion formed from excited 2-naphthol is quickly reprotonated; but as the pH increases the reprotonation rate constant k'_2 becomes smaller (and ϕ' increases from zero) until beyond pH3 reprotonation becomes negligible and ϕ/ϕ_0 settles down to the plateau value $1/(1 + k_1\tau_0)$ and ϕ'/ϕ'_0 to

$k_1\tau_0/(1 + k_1\tau_0)$, whence $k_1\tau_0$ is calculable directly. Along the plateau the fraction of excited 2-naphthol converted to naphtholate simply depends upon the ratio of the dissociation rate to the sum of all the rates for its disappearance, viz. $k_1/(k_1 + k_f + k_q + k_T)$ or $k_1/(k_1 + 1/\tau_0)$. At pH values near the ground state pK of 2-naphthol (9·5), further excited naphtholate appears because of its presence in the ground state, while at pH values just below the plateau region, where $k_2'\tau_0'$ becomes comparable to $k_1\tau_0'$, the analysis shows $k_2\tau_0'$ to be determinable also, e.g. from a plot of $(\phi/\phi_0)/(\phi'/\phi_0')$ against $[H^+]$ using (27). The Brønsted dependence of k_2 upon the ionic strength,

$$\frac{\phi/\phi_0}{\phi'/\phi_0'} = \frac{1}{k_1\tau_0} + \left(\frac{k_2\tau_0'}{k_1\tau_0}\right)[H^+] \qquad (27)$$

I, can be allowed for by plotting $[H^+]10^{z_B f(I)}$ instead of $[H^+]$, z_B being the charge on the base B and f(I) a function such as that of Davies (1962), $\sqrt{I}/(1 + \sqrt{I}) - 0·3I$, which reduces to $\sqrt{I}$ at low ionic strengths.)

From the fluorescence intensity measurements it is therefore possible to determine

$$\log_{10}(k_2\tau_0'/k_1\tau_0) = pK(S_1) + \log_{10}(\tau_0'/\tau_0) \qquad (28)$$

but the excited state pK can only be obtained if τ_0' and τ_0 are known.

The deprotonation of protonated 3-hydroxyquinoline is of the Case I type like 2-naphthol, but no plateau is observed (Fig. 3), presumably because $k_1\tau_0 \gg 1$ so that $k_1/(k_1 + 1/\tau_0)$ is almost unity. Since p$K(S_1) = -0·2$ (Haylock et al., 1963), it follows that $k_1 \sim 10^{10}$ s^{-1} and the condition $k_1\tau_0 \gg 1$ is likely to be satisfied.

Case II: the compound is in the B form in the ground state and this is the only form excited. Then $\rho_0 = 0$, $\rho_0' = 1$ and the equation corresponding to (27) is (29). Here the form of the fluorescence

$$\frac{\phi/\phi_0}{\phi'/\phi_0'} = \left(\frac{k_2\tau_0'}{1 + k_1\tau_0}\right)[H^+] \qquad (29)$$

intensity curves expected is always that of Fig. 3 (perhaps modified by quenching effects as in Fig. 4) and never of the 2-naphthol type with a plateau. Case II also differs from Case I in that variation of the pH cannot separate $k_2\tau_0'$ and $k_1\tau_0$; only $k_2\tau_0'/(1 + k_1\tau_0)$ can be

determined. If $k_1\tau_0 \gg 1$, the same result as for Case 1 becomes accessible, viz. (28); but extraneous information, such as an estimate of k_2 (Watkins, 1972a, b) coupled with values of τ_0 and τ_0', will generally be necessary to separate k_1 and k_2.

The pH at the half-way point on full "titration" curves of the Fig. 3 type, or on the similar curves approaching the plateau in Fig. 8, gives a simple indication of the $pK(S_1)$ in favourable cases. For compounds of either Case I or Case II type, the pH at the half-way point is $\log_{10}[k_2\tau_0'/(1 + k_1\tau_0)]$, which is only the same as $pK(S_1)$ if $\tau_0' = \tau_0$ and $k_1\tau_0 \gg 1$. Apart from the complication of the lifetime ratio, the half-way point on an emission "titration" curve can only be expected to correspond to the excited state pK-value if equilibrium is achieved in the protolytic reaction; i.e. k_1 and k_2' must be large compared with the rates of the decay processes, which sum to $1/\tau_0$ and $1/\tau_0'$ respectively, whence $k_1\tau_0 \gg 1$ and $k_2'\tau_0' \gg 1$. [The 1 in the denominator, or numerator, of equations like (25), (26), (27), or (29) always takes care of the extent to which failure to achieve equilibrium is important.]

If $k_1\tau_0 \ll 1$, the half-way point of a fluorescence "titration" curve must occur at a pH of $\log_{10}k_2\tau_0'$, which typically has a value ~ 2, corresponding to $k_2 \sim 10^{10}$ mole^{-1} dm^3 s^{-1} and $\tau_0' \sim 10^{-8}$ s. Thus reliance on the mid-point of "titration" curves is misleading for compounds with $pK(S_1)$-values much above 2 or 3, which may all appear to have $pK(S_1)$-values near 2 unless their B and BH$^+$ species have long lifetimes.
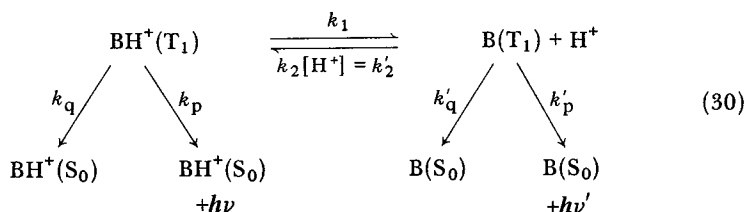
Even if equilibrium is achieved in the excited state, the lifetime effect always remains in emission intensity measurements. If the experimentally determined quantity on the left of (28) is regarded as the approximate $pK(S_1)$-value, the compound will appear to be a weaker acid than it really is i.e. too much BH$^+(S_1)$ will seem to be present if BH$^+(S_1)$ has the shorter lifetime, or a stronger acid if B(S_1) has the shorter lifetime. The rule is that the species of shorter lifetime produces a greater emission than would be expected from the equilibrium concentrations, because its concentration is depleted more rapidly and is therefore replenished all the time from the longer-lived species in an attempt to maintain the equilibrium.

Despite the fact that emission intensity measurements require supplementary lifetime determinations, they have the advantage over laser flash absorption techniques that they by-pass complications due to absorption by secondary products, such as radicals or solvated electrons (see e.g. Kläning *et al.*, 1973).

Triplet decay

When triplets are produced by conventional flash photolysis, with a flash on the μs timescale, so many singlet lifetime cycles are passed through and the timescale is relatively so long that both BH^+ and B may be found to some extent in the triplet state whichever form is present overwhelmingly in the ground state. Even in laser studies on the ns timescale, there will generally be some competition between the approach to the S_1 protolytic equilibrium and intersystem crossing. Thus in transposing the singlet scheme described above to the triplet reaction, it is even more necessary to allow for concentrations of both B and BH^+ forms to be present initially. The lifetimes of the triplets are usually so much longer than those of the singlets that these initial concentrations of $BH^+(T_1)$ and $B(T_1)$ can be taken as arbitrarily given, the fast initial processes involved in their build-up being ignored. At certain acidities the singlet lifetimes may nevertheless be sufficiently long for these initial triplet concentrations to reflect the equilibrium singlet concentrations of the acid and conjugate base forms; but when $pK(T_1)$ differs from $pK(S_1)$ the approach to the triplet equilibrium from the initial concentrations has still to be allowed for, even though the triplet lifetimes may be sufficiently long for the triplet equilibrium to be achieved over a much wider pH range.

Ignoring for simplicity other complications, such as radical formation, triplet-triplet annihilation, etc., the triplet scheme can therefore often be represented as (30). With triplet concentrations denoted by

$$
\begin{array}{ccc}
BH^+(T_1) & \xrightarrow[k_2[H^+]\,=\,k_2']{k_1} & B(T_1) + H^+ \\
{}_{k_q}\swarrow \quad \searrow{}_{k_p} & & {}_{k_q'}\swarrow \quad \searrow{}_{k_p'} \\
BH^+(S_0) \quad BH^+(S_0) & & B(S_0) \quad B(S_0) \\
\qquad +h\nu & & \qquad +h\nu'
\end{array} \tag{30}
$$

X and Y, the corresponding eqns to (13) and (14) are (31) and (32),

$$
\frac{dX}{dt} + AX = k_2' Y \tag{31}
$$

$$
\frac{dY}{dt} + A'Y = k_1 X \tag{32}
$$

where $A = (k_1 + k_p + k_q)$ and $A' = (k_2' + k_p' + k_q')$. The solutions are just like (15) and (16) but with X, Y, A, A', in place of x, y, a, a'. (Rayner and Wyatt, 1974). When the rate of acid dissociation is large compared with the rate of phosphorescence and radiationless processes, i.e. $k_1 \gg (k_p + k_q)$ or $(k_p' + k_q')$, neglect of small terms in the expansion

$$\sqrt{m} = (k_1 + k_2') + (k_p + k_q - k_p' - k_q')(k_1 - k_2')/(k_1 + k_2') \ldots$$

permits the simplification of the exact solutions to (33) and (34),

$$X = (k_1 + k_2')^{-1} \{(k_1 X_0 - k_2' Y_0)e^{-(k_1 + k_2')t} + k_2'(X_0 + Y_0)e^{-t/\tau}\}$$

$$(33)$$

$$Y = (k_1 + k_2')^{-1} \{(k_2' Y_0 - k_1 X_0)e^{-(k_1 + k_2')t} + k_1(X_0 + Y_0)e^{-t/\tau}\}$$

$$(34)$$

where

$$\frac{1}{\tau} = \frac{k_2'}{k_1 + k_2'} (k_p + k_q) + \frac{k_1}{k_1 + k_2'} (k_p' + k_q'). \qquad (35)$$

These equations are now easily interpreted. The first terms, in $\exp[-(k_1 + k_2')t]$, show the changes in X and Y due to the approach to the triplet protonation equilibrium, while the second terms, in $\exp(-t/\tau)$, describe the decay of the triplet population in terms of the lifetime τ. From (35) it can be seen that at high acidities, when k_2' is large, $1/\tau$ approaches $(k_p + k_q)$, while at low acidities it approaches $(k_p' + k_q')$, just as expected. Measurements of τ over the intermediate range of acidity can then lead to a determination of $K(T_1)$, i.e., of k_1/k_2. For example, eqn (35) can be thrown into the form (36), in

$$\frac{1}{\tau} = -K(T_1) \left[\frac{10^{-z_B f(I)}}{[H^+]} \left\{ \frac{1}{\tau} - (k_p' + k_q') \right\} \right] + (k_p + k_q) \qquad (36)$$

which the coefficient of $K(T_1)$ is determinable by experiment, the factor $10^{-z_B f(I)}$ allowing for the Brønsted dependence of k_2 on the ionic strength. As the signs show in (36), $1/\tau$ lies between $(k_p + k_q)$ and $(k_p' + k_q')$ and, if these should happen to be equal, (35) requires that $1/\tau$ will not alter with pH and $pK(T_1)$ will not be determinable in this way.

Chemical Complications

The above treatment gives some idea of a common pattern of the argument and of the scope of intensity and lifetime measurements. When other chemical processes have to be taken into account they can generally be incorporated into the schemes in a straightforward way and the resulting differential equations can be handled similarly. One of the simplest modifications arises in the treatment of acid-base reactions other than those involving the solvated proton. Thus Weller was able to investigate $pK(S_1)$ of acridine through its protonation by NH_4^+ at high pH, where protonation by H_3O^+ was negligible within the S_1 lifetime (Weller, 1957a). Hydrogen abstraction reactions, like that involved in the formation of naphthoxyl from naphthols, must also be expected as a complication in the interpretation of triplet transient spectra: thus a strong absorption at 465 nm due to the naphthoxyl radical has to be distinguished from the triplet absorptions when 2-naphthol is flash photolysed (Jackson and Porter, 1961).

Electrons can be ejected by ultra-violet light from aromatic molecules in solution (for a review, see Lesclaux and Joussot-Dubien, 1973). Recently Kläning *et al.* (1973) have reported that solvated electrons are formed from 2-naphthol by a 337·1 nm pulse from a nitrogen laser, and deduce that the rate of electron formation is higher than the rate of vibrational relaxation to the lowest excited singlet state. Since the electrons are relatively long-lived and take no further part in the ns time-scale reactions, the only effect they have upon the acid-base investigation is to necessitate a correction to the absorption spectra of the transient species under observation.

Physical Complications (1): Kinetic Behaviour
During the Approach to the Steady State

Many examples have now accumulated of chemical rate constants which have been found to agree well with the values predicted by Debye's equation for ionic encounters in solution (Debye, 1942), which, as is well known, requires encounter rate constants to be of the order 10^{10} dm^3 $mole^{-1}$ s^{-1} in water at 25°C. A review of the theory of encounter rates in general, with some reference to quenching mechanisms, has been given by Noyes (1961), and of

encounter rates with particular reference to acid-base excited state reactions by Weller (1961), who also gives a full account of tests of the application of Brønsted's theory of primary salt effects to such reactions.

Several investigators have given attention to the time dependence of rate parameters to be expected before steady-state conditions are established after a rapid perturbation. Förster (1951) pointed out that, when quenching of fluorescence simply depends upon the formation of an encounter complex between the quenching species and the excited state molecule, there will necessarily be some difference in behaviour between those molecules which find themselves in the vicinity of a quencher immediately upon excitation and those which do not. Those excited molecules which have a quencher within their "diffusion volume" are quenched so much more rapidly than those which do not that they may be omitted from the stationary state scheme for the dependence of fluorescence intensity upon quencher concentration; and the effect will show up because of the increasing importance of the correction with increasing concentration of quencher. At sufficiently low concentrations the chance of finding a quenching molecule in the diffusion volume of the excited species is negligible.

Weller has explored the implications of this effect upon acid-base equilibria, in which the diffusion-controlled nature of many protonation reactions obviously parallels that of quenching (Weller, 1957b, 1958a, 1961). He finds that the increased rate of the initial stages of the reaction can be accommodated by dividing the excited molecules into two parts, according to the presence or absence of a proton (or other reactant, such as OH^- etc.) in their diffusion volume, and treating them quite separately according to equations like (35) and (36). The separate contributions to ϕ/ϕ_0 and $\phi'\phi_0'$ are then finally summed. He gives two distinct examples of the application of this idea (Weller, 1958a):

(a) Reactions of the type (37). Here the excited HA* molecules are

$$HA^* + B \rightarrow A^{*-} + HB^+ \tag{37}$$

divided into one fraction, W_B, in the diffusion volume of which *no* B molecule is found, to which (25) and (26) are applied with $\rho_0 = W_B$ and $\rho_0' = 0$; and another fraction $1 - W_B$, in which the reaction is so fast that all HA* molecules belonging to this fraction can be regarded as converted initially to A^{*-}, i.e. $\rho_0 = 0$ and $\rho_0' = 1 - W_B$.

(*b*) Reactions of the type (38). In this case the argument is slightly

$$HA^* + H_2O \underset{k_2'}{\overset{k_1}{\rightleftharpoons}} A^{*-} + H_3O^+ \tag{38}$$
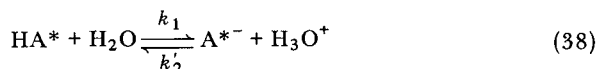
different. All the HA* molecules are surrounded by H_2O and are therefore at liberty to react at their normal rate, but those which have an H_3O^+ ion within their diffusion volume are assumed to be reconverted rapidly to HA* after dissociation and to have a negligible chance of dissociating again within their lifetime (so that, for this fraction, $k_1 = 0$). The fraction of HA* with *no* H_3O^+ in the diffusion volume is then treated as before with $\rho_0 = W_{H^+}$ and $\rho_0' = 0$; while the other fraction differs in having $\rho_0 = 1 - W_{H^+}$ and $\rho_0' = 0$ and, since $k_1 = 0$, $\phi/\phi_0 = 1 - W_{H^+}$ and $\phi'/\phi_0' = 0$ also for this fraction. Notice that $\rho_0' = 0$ for the whole population in this case.

Although this work was published some years ago, it is recalled here in order to point up a difference from a recent finding which at first sight appears to overlap. Ofran and Feitelson in their laser study of 2-naphthol (1973) found that their decay curves could only be made consistent with the known lifetime of 2-naphthol and 2-naphtholate if some 2-naphtholate was assumed to be present in the excited state initially, even though only the naphthol form could be excited from the ground state. There are two points of difference from the foregoing account: (i) the 2-naphthol reaction is of type (b) above, for which ρ_0 was set at zero for both fractions of excited HA*, while Ofran and Feitelson find $\rho_0' \neq 0$; (ii) in the Weller treatment the two parts of the reaction are dealt with quite separately, often with different assumptions about k_1 etc., and the ϕ/ϕ_0 contributions are summed at the end; the same result is not obtained in general by simply substituting values other than 1 or 0 for ρ_0 or ρ_0' into (25) and (26) for the reaction as a whole. Ofran and Feitelson do not actually compare their findings with the Weller treatment of initial reaction effects, but suggest that the explanation may lie in an initially greatly enhanced acidity of the 2-naphthol molecule when it finds itself surrounded by the ground state solvent arrangement before relaxation to that appropriate to the excited state.

Evidently we may look forward to more penetrating insights still into all these effects as the laser and single-photon counting techniques become further refined. It will obviously be very convenient if it always proves possible to justify the use of (35) and (36), and (15) and (16), with reasonable choices of ρ_0, ρ_0', x_0, and y_0.

Physical Complications (2): Adiabatic and Diabatic
Protonation Reactions

It has long been recognized (Jaffé and Jones, 1965; Schulman, 1973b) that there might be a difficulty in realizing excited state equilibria unless the states of the base and its conjugate acid are of the same type, when the proton can be attached or detached "adiabatically" (without the loss of excitation). It is clearly quite possible to imagine "diabatic" transitions, in which the electronic reorganization during the transfer of a proton to an excited base necessarily results in the production of the ground state protonated species. Indeed protonation of a molecule in the vicinity of a quencher with immediate de-excitation of the protonated form could sometimes constitute a reasonable quenching mechanism (Umberger, 1968). Latterly Förster has examined these possibilities from a theoretical point of view (Förster, 1970, 1973).

In general the relative possibilities of retention and loss of excitation during a proton transfer might be expected to depend upon several factors, among which the types of state involved may be important; but there seems no compelling reason to exclude the possibility of adiabatic proton transfers between states of different types, and there is some experimental indication that such transfers do take place (Ireland and Wyatt, 1973). From the practical point of view, however, effects of this kind may be accommodated by quenching terms in the foregoing algebra. The proportion of excited molecules which undergo diabatic proton transfers, ending up in the ground state, would count as being quenched either by protons when an $[H^+]$ dependent term appears in k'_q, (which then reads $k'_{q0} + k'_{H^+}[H^+]$), or by the solvent (or other base) when the effect is included in k'_q in the $BH^+(S_1)$ or $BH^+(T_1)$ dissociation schemes.

Cases of fluorescence quenching in acid solutions are quite common, but care is needed in their interpretation since at least part of the quenching effect may be due to the anions present (as can easily be demonstrated by adding salts to vary the anion concentration at a fixed acidity). Anion quenching effects have been recorded for some time (see e.g. Förster, 1951; Harriman and Rockett, 1973; Watkins, 1973) and are currently being interpreted in terms of the proximity of the excited state to higher charge-transfer states involving the anion (Watkins, 1973), thereby bringing them into line with charge-transfer mechanisms proposed for other quenchers (e.g. Weller, 1961: Carroll *et al.*, 1973). In some cases

however proton quenching, even of $B*H^+$ species, appears to occur (Umberger, 1968; Hussain and Wyatt, 1972).

The Rate Constants of Radiationless Transitions

Much more is becoming known about the rates of the physical processes in competition with proton exchange reactions in excited states. (For an excellent review see Henry and Siebrand, 1973.) The factors which determine the rate constants (k) for internal conversion and intersystem crossing are neatly summarized in the "Golden Rule" of time-dependent perturbation theory:

$$k = (4\pi^2/h)|H'_{mn}|^2\rho_m \tag{39}$$

Here h is Planck's constant, ρ_m is the density of states in the manifold to which the transition is occurring, and $|H'_{mn}|^2$ arises from the overlap of the wavefunctions of the initial and final states and depends upon both electronic and nuclear (vibrational) effects. Thus the much more rapid conversions between higher singlet states than from S_1 to S_0 are related to the large difference in the electronic energy gaps involved, conversions being more rapid the smaller the energy gap; and the lengthening of the lifetime of aromatic molecules by deuterium substitution is explained in terms of the poorer vibrational overlap in the CH bonds with the heavier isotope.

Other useful simple rules which emerge are that transitions should be more rapid from S_1 to a triplet state than from S_1 to the higher vibrational levels of the ground state (i.e., intersystem crossing from S_1 should be faster than internal conversion) and that intersystem crossing should be more rapid between $n\pi*$ and $\pi\pi*$ states than between states of the same type. Further, since the energy gap between S_1 and T_1 $n\pi*$ states is much less than that between those of $\pi\pi*$ states, intersystem crossing is faster between $n\pi*$ than $\pi\pi*$ states (unless T_2 also is involved).

4. SURVEY OF EXPERIMENTAL RESULTS

Reports of pK-values have appeared in increasing number since Weller's review (1961), and the relationship of this subject to analytical chemistry and biochemistry has led to a wide scattering of

information throughout the literature. Nevertheless, an attempt has been made here to gather together a reasonably comprehensive collection of $pK(S_1)$- and $pK(T_1)$-values. It has proved difficult in many

TABLE 1

Direction of the pK Change on Excitation for the Dissociation Reaction of Various Functional Groups

Reaction	$pK(S_1)$ $-pK(S_0)$	Example	Ref.
$-OH \rightleftharpoons -O^- + H^+$	Negative	1-Naphthol $pK(S_0) = 9\cdot2, pK(S_1) = 2\cdot0$	a
$-NH_2 \rightleftharpoons -NH^- + H^+$	Negative	2-Naphthylamine $pK(S_0) \geqslant 14, pK(S_1) = 12\cdot2$	b
$-NH_3^+ \rightleftharpoons -NH_2 + H^+$	Negative	2-Naphthylamine $pK(S_0) = 4\cdot1, pK(S_1) = -1\cdot5$	b
$\diagdown C=OH^+ \rightleftharpoons \diagdown C=O + H^+$	Positive	Xanthone $pK(S_0) = -4\cdot1, pK(S_1) = 1\cdot0$	c
$-CO_2H \rightleftharpoons -CO_2^- + H^+$	Positive	1-Naphthoic acid $pK(S_0) = 3\cdot7, pK(S_1) = 7\cdot7$	d
$-CO_2H_2^+ \rightleftharpoons -CO_2H + H^+$	Positive	1-Napthoic acid $pK(S_0) = -7\cdot7, pK(S_1) = 2\cdot0$	e
$-SO_3H_2^+ \rightleftharpoons -SO_3H + H^+$	Positive	1-Naphthalenesulphonic acid $pK(S_0) = -10\cdot6, pK(S_1) = -3\cdot7$	f
$-PO_3H_3^+ \rightleftharpoons -PO_3H_2 + H^+$	Positive	Phenylphosphonic acid $pK(S_0) = -6\cdot3, pK(S_1) = -2\cdot2$	g
$-AsO_3H_3^+ \rightleftharpoons -AsO_3H_2 + H^+$	Positive	Phenylarsonic acid $pK(S_0) = -5\cdot9, pK(S_1) = -2\cdot1$	g
$-NO_2H^+ \rightleftharpoons -NO_2 + H^+$	Positive	Nitrobenzene $pK(S_0) = -11\cdot3, pK(S_1) = 2\cdot3$	h
$Ar \diagdown NH^+ \rightleftharpoons Ar \diagdown N + H^+$	Positive	Acridine $pK(S_0) = 5\cdot5, pK(S_1) = 10\cdot6$	i
$\diagup \! C-H \rightleftharpoons \diagup \! C^- + H^+$	Negative	Fluorene $pK(S_0) = 20\cdot5, pK(S_1) = -8\cdot5$	j
$Ar \diagdown CH_2^+ \rightleftharpoons Ar \diagdown CH + H^+$	Positive	Naphthalene $pK(S_0) = -4\cdot0, pK(S_1) = 11\cdot7$	k
$-N=N- \rightleftharpoons -N=N- + H^+$ H^+	Positive	Azobenzene $pK(S_0) = -2\cdot90, pK(S_1) = 13\cdot7$	l

[a] Weller, 1958a.
[b] Förster, 1950.
[c] Ireland and Wyatt, 1972.
[d] Vander Donckt and Porter, 1968a.
[e] Watkins, 1972a.
[f] Yakatan and Schulman 1972.
[g] Liedke and Schulman, 1973b.
[h] Winefordner et al., 1971a.
[i] Weller, 1957.
[j] Vander Donckt et al., 1969b.
[k] Vander Donckt et al., 1970.
[l] Ellerhorst and Jaffé, 1968.