

# Effect of the Alkyl Group of Some Alcohols on the Proton-Transfer Reaction of 4-Methyl-2,6-diformylphenol and its Interaction with Triethylamine

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We have studied the effect of the alkyl group of some alcohols on the ground- and excited-state proton-transfer reaction of 4-methyl-2,6-diformylphenol (MFOH) at room temperature and 77 K by steady-state and nanosecond transient emission spectroscopy. It is observed that the proton-accepting abilities of the higher alcohols are different from those of lower alcohols and are dependent upon the size of the alkyl groups. The single Stokes-shifted emission observed in the visible region is assigned to a zwitterionic species which is converted into the phenolate anion (MFO<sup>-</sup>) in the presence of triethylamine. In the ground state MFO<sup>-</sup> is formed by the added base from the intramolecularly hydrogen-bonded closed conformer. From the excitation spectra it is proposed that MFOH can have more than one ground-state conformation. At 77 K the zwitterionic species is converted into the anionic conformer, changing the fluorescence into phosphorescence. From nanosecond measurements and the fluorescence quantum yield we have estimated the decay rate constants.

The static as well as dynamic processes involving intramolecularly hydrogen-bonded molecules are topics of current interest.<sup>1–10</sup> Nagaoka *et al.*<sup>11,12</sup> studied the structures and dynamic processes of the excited states of *o*-hydroxyacetophenone (OHAP), *o*-hydroxypropiophenone (OHPP) and *o*-hydroxybenzaldehyde (OHBA). They have shown that the main species existing in the excited state in alcohols are intermolecularly hydrogen-bonded open conformers which phosphoresce at low temperature. Smith *et al.*<sup>13</sup> and Acuña *et al.*<sup>14</sup> have suggested a zwitterionic structure for S<sub>1</sub> states of methyl salicylate. However, Forster<sup>15</sup> pointed out that the spectral changes which occur in aromatic hydroxy compounds are due to complete proton transfer to solvents like alcohols and water. In alcohols different structural forms of the solute molecules are available owing to solute–solvent interactions. In a relatively weak hydrogen-bonding solvent the observed absorption and emission spectra are due to superposition of different absorptions and emissions resulting from different structural forms which may bring their energy gap close together.<sup>16</sup> These structural forms may be reflected only in the excitation spectra. In our previous works it was shown that large Stokes-shifted fluorescence originates from the enol tautomer of 4-methyl-2,6-diformylphenol (MFOH) in hydrocarbon solvents<sup>17</sup> and

from the anion in ethanol.<sup>18</sup> In order to obtain further information about the nature of the species present, we have examined the spectral properties of MFOH in some higher alcohols such as propanol, butanol, isobutanol, isopropanol and pentanol in the absence and presence of triethylamine (TEA) at room temperature and at 77 K in comparison with ethanol. The alkyl groups in alcohols have a positive effect and are able to release electrons towards the oxygen atom so that it becomes rich in electron density. This enhanced electron density on the oxygen atom makes the alcohols proton acceptors. We have also studied the fluorescence decay of MFOH by nanosecond spectroscopy in order to determine the decay rates and have discussed the decay properties in comparison with other related compounds. In addition we have studied the nonradiative rates as a function of dielectric constant of the alcohols.

## Experimental

MFOH is prepared and purified as described earlier.<sup>17</sup> The solvents ethanol, propanol, butanol, isopropanol, isobutanol, pentanol and hexanol were all of spectroscopic grade (Fluka) and were freshly distilled before use. The solvents were routinely stored over 3 Å molecular sieves before use. Triethylamine (TEA) was from Merck

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(Schuchardt) and was used as received. Absorption spectra were measured on a Jasco model 7850 UV/VIS spectrophotometer and fluorescence spectra on a Perkin-Elmer MPF 44B spectrofluorimeter. Fluorescence lifetime measurements were carried out in an SP 70 nanosecond spectrometer (Applied Photophysics Ltd., UK) using a pulsed nitrogen lamp, based on the time-correlated single-photon counting technique (TCSPC). The instrument response function was found to be 1.6 ns at full width at half maximum ( $\text{FWHM} \approx 1.6$  ns). MFOH solutions were degassed for 10 min prior to the study of low-temperature emission. The low-temperature emission was recorded using a quartz glass dewar and liquid nitrogen. The concentrations of MFOH solutions were maintained at  $(3-6) \times 10^{-5}$  mol  $\text{dm}^{-3}$ . Relative quantum yields are determined by comparison with a standard (fluorescin:  $\phi_f = 0.9$ ) as described earlier.<sup>19,20</sup> The fluorescence intensities were corrected by subtracting the intensities from the sample blanks. This corrected for any signal from scattered light or emission from impurities.

## Results and discussion

**Spectral features at room temperature.** The absorption spectra of MFOH taken in different alcoholic solvents at a fixed concentration of MFOH and in the presence of TEA are shown in Fig. 1. The blue band (350 nm) is similar to that in nonpolar solvents<sup>17</sup> and is attributed to an intramolecularly hydrogen-bonded closed conformer (I, Scheme 1). From Fig. 1 it is evident that the population of the species responsible for the appearance of the absorption band at 440 nm is distinctly dependent upon the nature of the alcohols used. Above a certain concen-

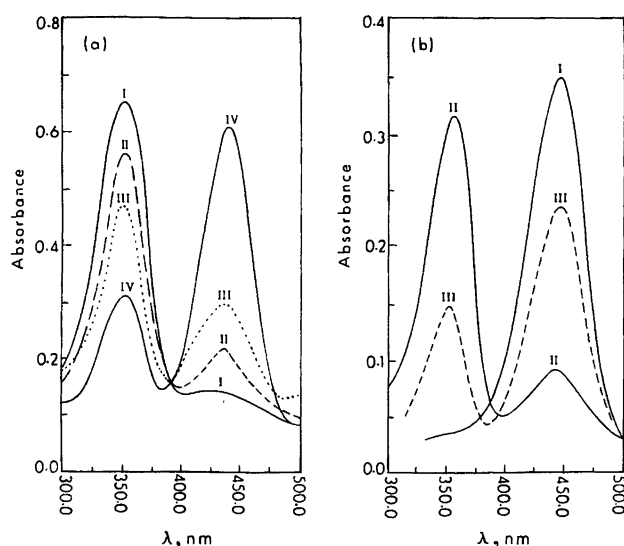
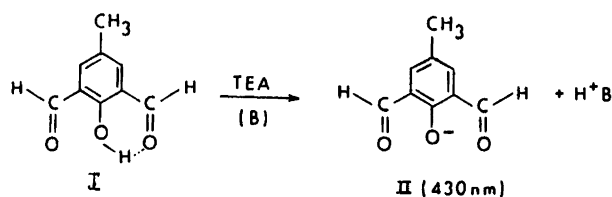
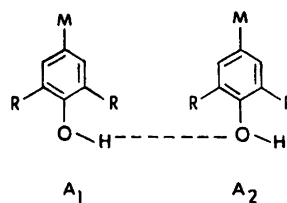
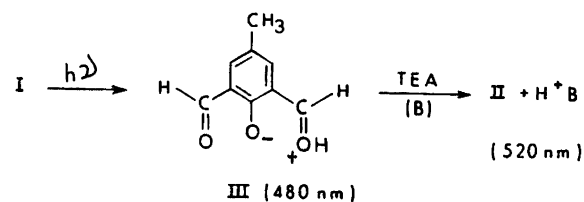


Fig. 1. Absorption spectra of MFOH in the absence (a) and presence (b) of TEA.  $[\text{MFOH}] = 5.0 \times 10^{-5}$  mol  $\text{dm}^{-3}$  and  $[\text{TEA}] = 4.5 \times 10^{-4}$  mol  $\text{dm}^{-3}$ . (a) (I) pentanol, (II) butanol, (III) propanol and (IV) ethanol. (b) (I) ethanol, (II) butanol, (III) propanol.

### Ground state



### Excited state



Scheme 1. M and R denote  $-\text{CH}_3$  and  $-\text{CHO}$ , respectively.

tration of MFOH ( $6 \times 10^{-5}$  mol  $\text{dm}^{-3}$ ), the long-wavelength absorption band at 440 nm is not observed in any of the solvents except ethanol. However, in a very dilute solution (below  $6 \times 10^{-6}$  mol  $\text{dm}^{-3}$ ) of MFOH this absorption band at 440 nm appeared in addition to the stronger blue band even in butanol, isobutanol and pentanol. However, on addition of TEA, the long-wavelength band appears even in ca.  $10^{-5}$  mol  $\text{dm}^{-3}$  solution and continues to increase with the increase in concentration of base in all the solvents studied here. In our earlier study<sup>18</sup> MFOH shows dual absorption bands at 350 and 430–440 nm in ethanol, respectively. In analogy with our observations in hydrocarbon solvents,<sup>17</sup> the 350 nm band in ethanol was assigned as due to the intramolecularly hydrogen-bonded closed conformer of MFOH (I, Scheme 1). Upon addition of a base (TFA) the intensity of the 430–440 nm band in ethanol increases with a concomitant decrease in intensity of 350 nm band. This observation indicates that the 440 nm band in ethanol is due to the corresponding phenolate anion (MFO<sup>-</sup>) II in Scheme 1. Therefore, this long-wavelength absorption band in higher alcohols is assigned as due to the MFO<sup>-</sup> anion. From these observations it is evident that in the ground state the extent of the intermolecular proton transfer (IMPT) reaction of MFOH with solvent has markedly decreased in higher alcohols compared with that in ethanol. The fluorescence spectra exhibit a large Stokes-shifted band at 480–490 nm in all the higher alcohols. On

the other hand, in ethanol and water a single emission band appears at 520 nm.<sup>18</sup> The intensity of this band at 520 nm increases without any change in its position by the addition of a base. This fact indicates that the emission band at 520 nm in ethanol and water must have resulted from the phenolate anion ( $\text{MFO}^-$ ) anion.<sup>18</sup> On addition of TEA the 480–490 nm emission band in the higher alcohols shifts to 520 nm, and the intensity of this 520 nm band continues to increase with the gradual addition of TEA, i.e. the anion is formed in the presence of a strong base like TEA (Fig. 2a). These observations can be explained on the basis of a different type of solute/solvent interaction in these higher alcohols from that in ethanol. It is shown earlier that complete transfer of the proton is possible only in ethanol in the excited state. It seems, therefore, that the base is acting as a promoter for ionization to the solvent in these higher alcohols. The visible emission band may be assigned as due to the zwitterion<sup>21</sup> of MFOH (**III**, Scheme 1), which is converted into the anion on addition of a base. On the other hand, the emission spectra of *o*-methoxybenzaldehyde appear in the 380–400 nm region in *n*-hexane and pentanol. This substantiates evidence of the fact that the 480 nm emission is not due to the normal compound.

It therefore seems that in a medium of weak proton-accepting ability the zwitterionic species exists, while in a highly polar medium such as ethanol and methanol intermolecular proton translocation or ionization is likely to occur. Thus we come to the conclusion that higher alcohols are weakly proton-accepting compared to methanol and ethanol. This must be due to the presence of bulky alkyl groups in these higher alkanols. Since in

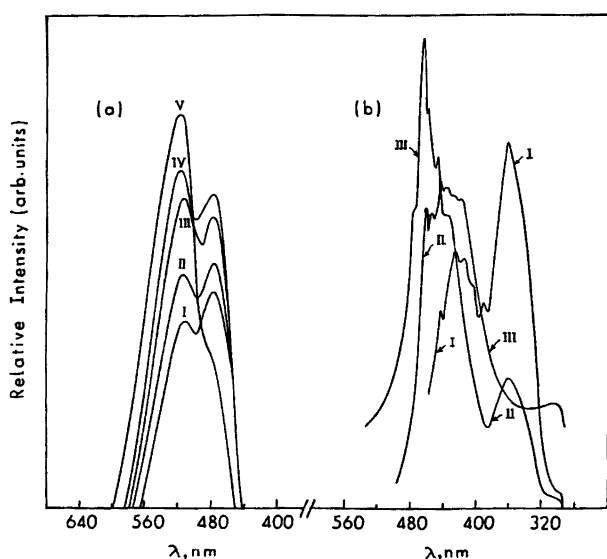


Fig. 2. Room-temperature fluorescence spectra of MFOH in propanol. (a) emission spectra with varying concentration of TEA ( $\text{mol dm}^{-3}$ )  $\times 10^{-4}$ : (I) 3.2, (II) 4.5, (III) 5.2, (IV) 6.8 and (V) 9.5. (b) Excitation spectra: (I) and (II) monitored at 480 and 520 nm, respectively, and (III) in the presence of TEA monitored at 520 nm.

the excited state the carbonyl group becomes more basic and the hydroxyl group more acidic, it seems quite reasonable that partial negative and positive charges have developed due to some sort of electronic interaction. A model that can rationalize the above results may be represented in Scheme 1 as  $\text{I} \rightarrow \text{III} \rightarrow \text{II}$ . In this case the immediate precursor to IMPT may be assigned to species **III**, which is considered to originate from the ground-state closed conformer **I** under this particular experimental condition and **III** can undergo IMPT in the presence of a base even in these higher alcohols. The excitation spectra obtained by monitoring the emissions at 480 and 520 nm, in both the absence and presence of TEA, are different from each other as shown in Fig. 2b, and none can explain the ground-state closed conformation. The different excitation spectra indicate the presence of more than one species in the ground state. The excitation spectra obtained by monitoring the emission at 520 nm appeared at 450 nm in pure solvent as well as in the presence of TEA and are broadly structured, indicating the complex nature of the spectra and the presence of more than one species, as was observed earlier.<sup>12,22</sup> The excitation spectra show that a band at 430 nm obtained by monitoring the 480 nm emission is indeed similar to the 440 nm absorption band obtained in the presence of base. However, excitation spectra of MFOH in higher alcohols are different from those in ethanol, as shown earlier.<sup>18</sup> In the excited state carbonyl groups become more basic and hydroxyl groups become more acidic. This change in acid–base properties causes tautomerization. However, tautomerization is not expected to occur in these protic solvents owing to the strong intermolecular interaction of MFOH with the solvent medium,<sup>23</sup> although these solute/solvent interactions are relatively weak in higher alcohols compared to ethanol. In some similar studies with methyl salicylate, Smith *et al.*<sup>13</sup> and Acuña *et al.*<sup>14</sup> have suggested zwitterionic structure in an environment where proton activity is low.<sup>21,24</sup> All these observations imply that MFOH could be partially or completely ionized in pure water and ethanol, both in the ground and excited state, but can not be ionized so easily in higher alcohols under the same experimental conditions even in the excited state. We have shown that this ionization effect is a maximum in ethanol and a minimum in pentanol. The most probable reasons are given below:

(i) The bulky alkyl groups of higher alcohols prevent the solvent molecules from coming into the vicinity of the hydroxy proton to form an efficient intermolecular hydrogen bond, which can be considered to be the first step of IMPT. Accordingly, these higher alcohols are weakly proton accepting compared to ethanol. In a recent study Yao *et al.*<sup>25</sup> also made similar conclusions.

(ii) It is well established that the alkyl group chain is quite flexible at room temperature. Therefore, the inductive effect due to the alkyl group should also play an important role in the IMPT reaction of MFOH with these solvents.

(iii) The dielectric constant of ethanol (24.6) is higher than those of butanol (17.1), isobutanol (15.8), pentanol (13.9) and hexanol (13.3). The proton-accepting ability of weakly polar solvents should be lower than that of more polar solvents, i.e. ionization is sensitive to the proton-accepting ability and polarity of the medium. All the above facts show that ethanol is the strongest proton-accepting solvent among *n*-alkanols.

(iv) We have analyzed the concentration dependence of the absorption spectra of MFOH in all the solvents studied here. The appearance and disappearance of the absorption band due to the variation in concentration of MFOH indicates dimer formation. The phenols, aromatic acids, form a stable dimer in solution.<sup>8</sup> This dimerization is relatively less in ethanol, and even in butanol and pentanol, and in relatively more dilute solution, ca.  $10^{-6}$  mol dm<sup>-3</sup>. It is likely that dimeric forms are also present in the more abundant intramolecularly hydrogen-bonded monomer of MFOH (350 nm). Dimerization does not favour ionization. The population of the dimer should be higher in relatively weak polar solvents such as pentanol and butanol. In ethanol below ca.  $5 \times 10^{-5}$  mol dm<sup>-3</sup> solution of MFOH only the band at 440 nm is observed. This is clearly a solvated anionic monomer of MFOH in ethanol. Therefore, complete transfer of a proton is possible in ethanol at this concentration of MFOH. It is suggested earlier that phenol monomer and dimers have different probabilities of dissociative ionization,<sup>26-28</sup> and phenol dimer should be blue-shifted relative to the monomer. Recently Steadman and Syage<sup>29</sup> have shown that dimerization hinders the reaction significantly relative to the monomer and the dimer self-association prevents the solvent from acting as a proton acceptor. The intermolecular proton transfer (IMPT) in weakly solvated medium (butanol and pen-

tanol) is inhibited owing to the formation of dimers of the A<sub>1</sub> and A<sub>2</sub> type (Scheme 1). The A<sub>1</sub> dimer has a restricted proton, which should quench the ground-state IMPT to the solvent. A<sub>2</sub> has a free proton available to the solvent. Both types are expected to be red-shifted by solvation with TEA. We observed a red-shifted absorption and in the presence of TEA. The most favourable bonding site for solvent molecules (or TEA) is that which surrounds the type A<sub>2</sub> proton, thus facilitating the IMPT. In the case of azaindole, Bayoumi *et al.*<sup>30</sup> pointed out that dimerization should not take place in ethanol. In a similar study Barbara *et al.*<sup>26</sup> pointed out that dimers are only stable in a limited range of concentration of the conformer and the solvents. Therefore the long-wavelength absorption band in butanol and pentanol disappears at higher concentrations of MFOH due to dimer formation. Finally the intramolecular hydrogen bond in MFOH is stronger than an intermolecular hydrogen bond with such weakly proton-accepting solvents. Hence, stronger intramolecular hydrogen bonding would not be expected to be interrupted in these higher alcohols.

*Fluorescence decay at room temperature.* To obtain further information on the effect of these alcoholic solvents on the proton-transfer reaction of MFOH in the excited state we have analysed the fluorescence decay of MFOH in pure solvents and in the presence of TFA. The decay shows a single exponential fit (Fig. 3). We obtained single lifetimes ( $\tau_f$ ) even in the presence of TEA (Table 1). It is observed that  $\tau_f$ -values are not affected much by the presence of bulky alkyl groups of these alcohols (Table 1). From the nanosecond measurements and quantum yield of fluorescence ( $\phi_f$ ) we have estimated the radiative ( $k_f^r$ ) and nonradiative ( $k_f^{nr}$ ) decay rate constants from eqns. (1) and (2).

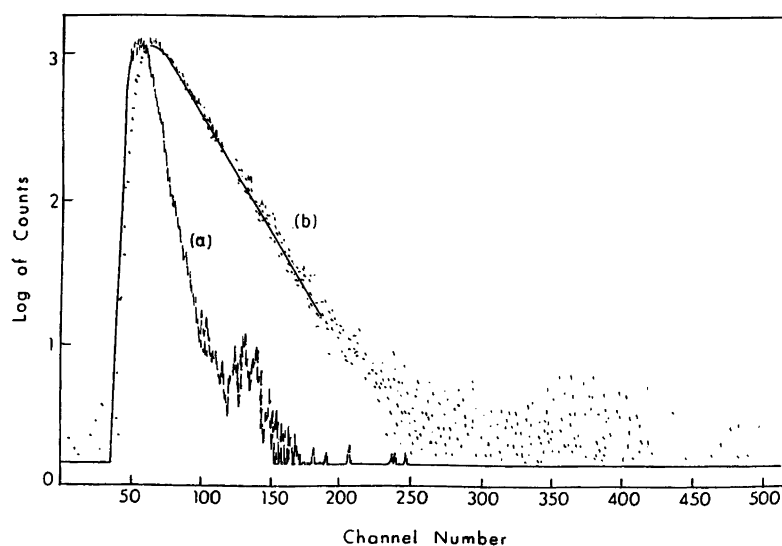


Fig. 3. Fluorescence decay profile of MFOH in pentanol at room temperature; emission wavelength at 490 nm (resolution 0.166 ns/channel). (a) Lamp profile (Instrument response function of nitrogen lamp); (b) the computed best fit (solid line) of the experimental points to a single exponential decay.

**Table 1.** Fluorescence quantum yield ( $\phi_f$ ), lifetime ( $\tau_f$ ) and decay rate constants ( $k_f^r, k_f^{nr}$ ) of MFOH fluorescence.

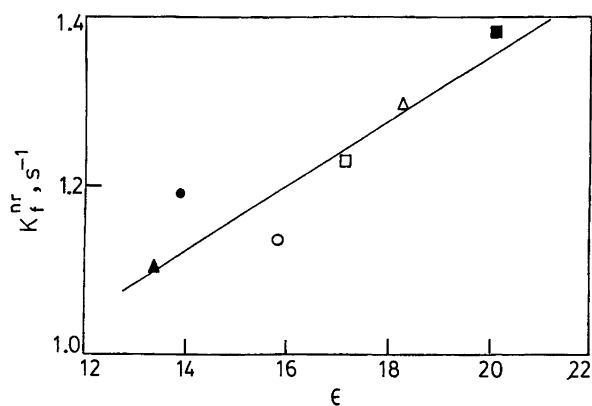
Solvent	$\phi_f$	$\tau_f/\text{ns}$	$k_f^r/\text{s}^{-1} \times 10^{-7}$	$k_f^{nr}/\text{s}^{-1} \times 10^{-8}$
Ethanol	0.4	5.5	7.2	1.1
Pentanol	0.29(0.59)	5.7(4.5)	5(13.1)	1.2(0.9)
Hexanol	0.25(0.55)	5.5(4.2)	4.5(13.0)	1.3(1.1)
Butanol	0.28(0.59)	5.7(4.6)	1.2(1.0)	
Isobutanol	0.34(0.67)	5.7(4.6)	5.9(14.5)	1.1(7.2)
Propanol	0.23(0.48)	5.5(4.9)	4.1(9.7)	1.4(1.0)
Isopropanol	0.26(0.56)	5.7(4.5)	4.5(12.4)	1.3(0.9)
<i>n</i> -Hexane	0.1	1.4	7.1	6.4

$\lambda_{\text{exc.}}$  (for  $\phi_f$ )=360 nm; the values in parentheses are in the presence of base (520 nm emission).

$$1/\tau_f = k_f = k_f^r + k_f^{nr} \quad (1)$$

$$\phi_f/\tau_f = k_f^r \quad (2)$$

Results are displayed in Table 1. The values of rate constants in Table 1 show that proton transfer in MFOH is a slow process. In the case of methyl salicylate and related compounds, Acuna *et al.*<sup>24</sup> pointed out that if zwitterionic structures are really responsible for Stokes-shifted emission then proton translocation in the excited state should be slow. This is in favour of a zwitterionic conformation of MFOH in the excited state. The relatively slow decay rates in butanols and pentanol (Table 1) from that in hydrocarbon solvents<sup>17</sup> ( $k_f = 9.1 \times 10^{-8} \text{ s}^{-1}$  in cyclohexane) indicate the presence of a solvent-induced barrier. Figure 4 shows the relationship between dielectric strength of the higher alcohols and the non-radiative decay rate of MFOH. The data show that there is a good correlation between dielectric strength of the solvent and nonradiative decay rate of MFOH. In a similar study Smith and Kaufmann<sup>21</sup> observed higher dielectric strength solvents to yield higher nonradiative rates. On this basis they suggested zwitterionic structure of methyl salicylate for the fluorescing species. In our case, however, this is valid only in the case of higher alcohols. Figure 4 shows a similar correlation between  $k_f^{nr}$  and  $\epsilon$

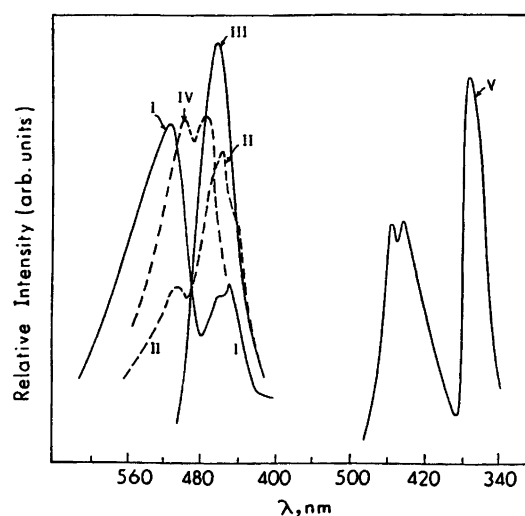


**Fig. 4.** Relationship between the dielectric strength ( $\epsilon$ ) of the solvents and the nonradiative decay rate,  $k_f^{nr}$ , of MFOH: (●) pentanol, (○) isobutanol, (□) butanol, (△) isopropanol, (■) propanol and (△) hexanol.

which validates zwitterionic species of MFOH being fluorescent in the excited state ( $S_1$ ).

#### Low-temperature fluorescence and phosphorescence spectra.

The emission and excitation spectra of MFOH at 77 K are shown in Fig. 5. The emission spectra at 77 K consist of a visible fluorescence band and a stronger yellow phosphorescence. The phosphorescence intensity decreases as the excitation wavelength is increased or the temperature is raised, and the visible emission is observed only at room temperature or when excited by low-energy light. The decrease in phosphorescence intensity at higher temperature is simply due to temperature-dependent quenching. The presence of phosphorescence spectra indicates the presence of intersystem crossing (ISC), resulting in triplet-state population. The  $T_1$  states of benzaldehyde-type molecules are  $^3n\pi^*$  in character in nonpolar and  $^3\pi\pi^*$  in protic polar solvents.<sup>11,12</sup> Accordingly, the zwitterionic or partially ionized species of MFOH may undergo ISC to the triplet state.<sup>21</sup> The strong phosphorescence observed in these solvents shows that ISC is a probable deactivation mechanism for the singlet zwitter-



**Fig. 5.** Emission (I–IV) and excitation (V) spectra of MFOH in butanol at 77 K:  $\lambda_{\text{exc}}$  nm = (I) 360, (II) 380, (III) 400, (IV) in the presence of TEA, 350, and (V) phosphorescence excitation spectra monitored at 520 nm.

ion or partially ionized species. The phosphorescence excitation spectra (Fig. 5) are similar to the room-temperature absorption spectra. An interesting observation is that at 77 K in the presence of a base, the emission spectra split into two peaks when excited with 350 nm light (Fig. 5, IV). The peaks are close to each other and therefore must be due to two different vibronic levels, as was observed earlier.<sup>17</sup> The appearance of phosphorescence spectra of MFOH in these solvents indicates that the triplet state becomes populated.

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