$$\mathrm{Cp^*{}_2Ta(\eta^2\text{-}O_2)CH_3 + P(C_6H_5)_3 \rightarrow Cp^*{}_2Ta(O)CH_3 + OP(C_6H_5)_3} \quad (6)$$

equiv) are not oxidized (days 80 °C). An interesting phenomenon was noted while carrying out these reactions. When heated to 80 °C in the presence of triethylamine $\mathrm{Cp^*{}_2Ta(\eta^2\text{-}O_2)CH_3}$ does *not* decompose; isonitrile significantly slows its decomposition. In contrast, when $\mathrm{Cp^*{}_2Ta(\eta^2\text{-}O_2)CH_3}$ is heated in solution alone, or in the presence of styrene or CO, a (non-first-order) rearrangement to $\mathrm{Cp^*{}_2Ta(O)OCH_3}$ occurs. Trace amounts of acid, possibly on the surface of the glass NMR tube,[11] might serve to catalyze the observed rearrangement. Indeed, addition of even trace amounts of methanesulfonic acid greatly accelerates methyl migration to oxygen (eq 7).

$$\mathrm{Cp^*{}_2Ta(\eta^2\text{-}O_2)CH_3 \xrightarrow{[H^+],\ 80\ ^\circ C} Cp^*{}_2Ta(O)OCH_3} \quad (7)$$

The reactivity of the phenyl derivative is similar to that for the methyl, except that trace acid is required to oxidize triphenylphosphine.[12] Addition of 1 equiv of $\mathrm{R'SO_3H}$ ($\mathrm{R' = CH_3, C_6H_4CH_3}$) to $\mathrm{Cp^*{}_2Ta(\eta^2\text{-}O_2)R}$ ($\mathrm{R = CH_3, CH_2CH_3, CH_2CH_2CH_3, CH_2C_6H_5}$) leads to the corresponding alcohol (ROH) and what appears to be $\mathrm{Cp^*{}_2Ta(O)OSO_2R'}$ over a period of 3 days at 25 °C. Initial indications were that other Lewis acids, e.g., $\mathrm{AlR_3}$,[13] will also promote the rearrangement shown in eq 7.

$$\mathrm{Cp^*{}_2Ta(O_2)R + R'SO_3H \rightarrow Cp^*{}_2Ta(O)OSO_2R' + ROH} \quad (8)$$

Electrophilic attack at the exo-oxygen atom would enhance heterolysis of the O–O bond during migration of the alkyl (or phenyl) group (Scheme I). Similarly, nucleophilic attack at the endo-O by phosphines or sulfur dioxide would be enhanced when Lewis acids are coordinated to the exo-oxygen atom. This mechanism for the acid-catalyzed rearrangement of $\mathrm{Cp^*{}_2Ta(\eta^2\text{-}O_2)R}$ to $\mathrm{Cp^*{}_2Ta(O)OR}$ is reminiscent of the mechanism proposed for the rearrangement of the isoelectronic $\mathrm{Cp^*{}_2Hf(OOCMe_3)(R)}$ to $\mathrm{Cp^*{}_2Hf(OCMe_3)(OR)}$, where $\mathrm{[CMe_3]^+}$ formally serves the role of the electrophile in Scheme I.[6]

The clean nature of these rearrangements as well as the promotion by Lewis acids indicates a *dipolar* character for intramolecular or bimolecular attack at $\mathrm{M(\eta^2\text{-}O_2)}$ concurrent with O–O bond cleavage, which proceeds by interaction of the migrating (or in-coming) group's electron pair with the activated σ^* orbital of the [O–O] moiety. This dipolar reactivity reveals potentially very different reaction patterns for these metal peroxides as compared with free-radical autoxidations.

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Supplementary Material Available: Experimental details describing the syntheses of $\mathrm{Cp^*{}_2Ta({=}CHC_6H_5)H}$, $\mathrm{Cp^*{}_2Ta(\eta^2\text{-}C_6H_4)H}$, and $\mathrm{Cp^*{}_2Ta(\eta^2\text{-}O_2)R}$ and tables of crystal structure parameters, final parameters, bond distances and angles, hydrogen parameters, and anisotropic displacement parameters (13 pages); tables of observed and calculated structure factors for $\mathrm{Cp^*{}_2Ta(\eta^2\text{-}O_2)CH_2C_6H_5}$ (20 pages). Ordering information is given on any current masthead page.

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(11) Prior rinsing of the NMR tube with KOH/isopropyl alcohol results in a much slower rate of decomposition.

(12) Acid promotion in the transfer of oxygen from metal peroxides to triphenylphosphine has been noted previously: Mimoun, H.; Perez-Machirant, M. M.; Seree de Roch, I. *J. Am. Chem. Soc.* **1978**, *100*, 5437.

(13) These reactions appear to be more complex due to alkyl/alkoxide exchange between aluminum and tantalum. For example, treatment of $\mathrm{Cp^*{}_2Ta(\eta^2\text{-}O_2)CH_2CH_2CH_3}$ with $\mathrm{Al(CH_2CH_3)_3}$ affords the adduct $\mathrm{Cp^*{}_2Ta(O)(CH_2CH_3){\cdot}Al(CH_2CH_3)_2(OCH_2CH_2CH_3)}$.

Intramolecular Charge-Transfer Transition in Benzanilides and Its Dielectric Medium Modulation

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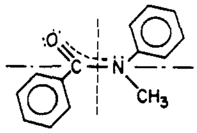
The fluorescence spectrum of benzanilide exhibits the anomaly that its λ_{max} occurs at longer wavelengths than that of its phosphorescence emission.[1] Recently, Tang, MacInnis, and Kasha[2] interpreted this anomaly on the basis of a proton-transfer fluorescence $S_1' \rightarrow S_0'$ of the imidol tautomer transient. A test of a proton-transfer mechanism is the methylation of the molecule at the sensitive proton position. We have now studied the *N*-methylbenzanilide (I) and were surprised to observe a fluorescence in the 500-nm region, Figure 1 (curve 1, onset 450 nm, λ_{max} 510 nm, MCH, 298 K).



I

(trans)-N- METHYLBENZANILIDE

The UV absorption spectrum shows moderate to strong absorption starting at 310 nm. The weak fluorescence observed from 300 to 400 nm (Figure 1) must arise from a weak absorption band, corresponding to excitation in a locally excited moiety (structure I), buried in the stronger $S_1(\pi\pi^*) \leftarrow S_0$ absorption with $\lambda_{max} \sim 250$ nm, $\epsilon = 10\,000$ $\mathrm{M^{-1}\,cm^{-1}}$.[1] This is supported by the suggestive band contour (exceptional long wavelength tail), the strongly competitive excitation of the $T_1 \rightarrow S_0$ emission, and the resolved and discrete weak absorption observed[3] in benzamide (λ_{max} 270 nm, $\epsilon \sim 600$ $\mathrm{M^{-1}\,cm^{-1}}$).

The long wavelength fluorescence band at 510 nm must result from an intramolecular charge-transfer transition which involves the whole molecule. Such charge-transfer fluorescence bands with large wavelength shifts have been characterized as *twisted intramolecular charge-transfer* emissions in dimethylanilines and have been studied for many different molecular structures.[4] Such intramolecular CT transitions have not been suspected previously for benzanilides. The absence of a *direct absorption* to the charge-transfer state is an indication of the indirect relaxation mechanism by which the state is excited. This mechanism involves internal torsion (cf. structure I) and dielectric relaxation. One test of the charge-transfer nature of the fluorescence is the sensitivity of the band to dielectric medium effects. The 510-nm band for *N*-methylbenzanilide (and the corresponding one for benzanilide) does shift strongly with changes in dielectric constant, with $\Delta\bar{\nu} = 1080$ $\mathrm{cm^{-1}}$ for the change from *n*-heptane ($\epsilon = 1.92$) to tetrahydrofuran ($\epsilon = 7.39$); the comparable shift for anthracene π,π^* fluorescence is 118 $\mathrm{cm^{-1}}$. Parallel behavior is observed with empirical solvent polarity indices, such as the E_T index,[5] although the values of E_T available are limited.

If a strongly dipolar solvent is used, e.g., ethyl alcohol or propylene oxide, the 510-nm fluorescence is quenched, and the normal short wavelength fluorescence is strengthened. A specific dipole–dipole complex can block the charge-transfer excitation by severely polarizing one end of the heteromolecule.

[†] On leave of absence from the Institute of Experimental Physics, University of Gdańsk, 80-952 Gdańsk, Poland.

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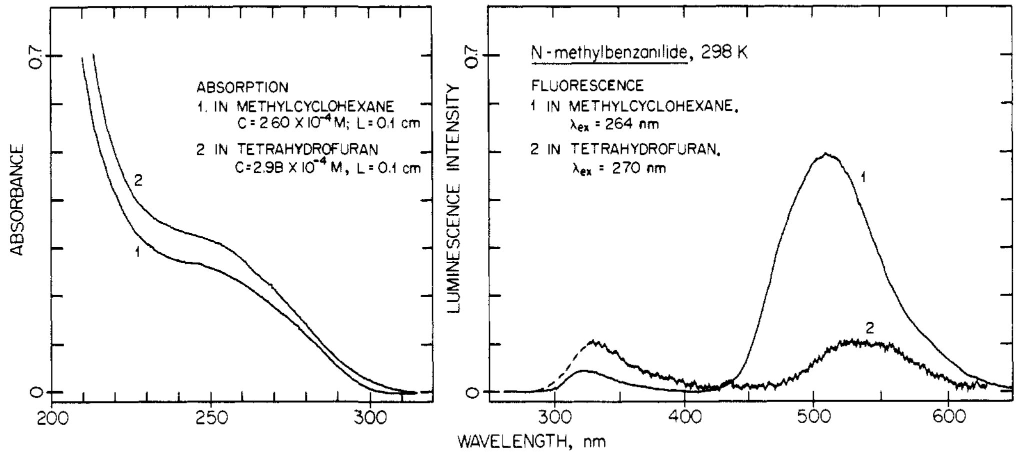

Figure 1. Spectra of *N*-methylbenzanilide in solution at 298 K.

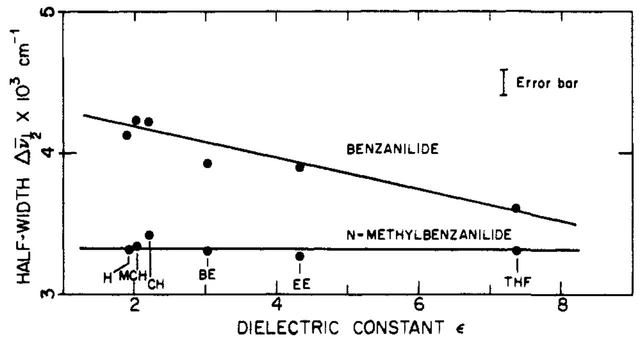

Figure 2. Spectroscopic half-width (FWHM) of 500-nm region fluorescence bands of benzanilides at 298 K. Solvents H (hexane), MCH (methylcyclohexane), CH (cyclohexane), BE (dibutyl ether), EE (diethyl ether), THF (tetrahydrofuran).

The fluorescence spectra of benzanilide compared with those of *N*-methylbenzanilide, however, reveal an additional complexity in the former. First of all, the half-width of the green fluorescence of benzanilide (onset 400 nm, λ_{max} 475 nm, MCH at 298 K) proves to be substantially greater than that of *N*-methylbenzanilide, $\Delta\bar{\nu}$ = 4115 cm^{-1} vs 3316 cm^{-1}. Secondly, the benzanilide fluorescence half-width markedly contracts as the dielectric constant increases from 1.92 (H) to 7.39 (THF), whereas, the *N*-methylbenzanilide fluorescence half-width remains constant. Figure 2 gives a plot of fluorescence band half-width (FWHM) versus dielectric constant for various solvents; a parallel behavior is observed for the E_T index.[5] These and related observations[6] suggest that *in benzanilide the observed blue-green fluorescence band consists of two independent overlapping fluorescence in hydrocarbon solution at 298 K.* Thus, the report by Tang, MacInnis, and Kasha[2] interpreting the long wavelength fluorescence as being of proton-transfer tautomer origin is supported in part. Recently Tang confirmed the presence of H-bonding dimer formation in benzanilide by infrared spectral studies,[7] adding confidence to the H-bonded dimer proton-transfer mechanism proposed earlier.[2]

The photochemical study of benzanilide and related molecules[8-10] and the striking rearrangements observed require a detailed understanding of the electronic excited states giving rise to the photochemical products. The initial fluorescence anomaly reported by O'Connell et al.[1] has proved to be unusually subtle. The present study has been extended in several directions, most particularly to picosecond dynamics. These latter results confirm three modes of depopulating the initially excited singlet state, as evidenced by the steady-state spectroscopy studies presented here. A comprehensive paper on these and related results is in preparation.

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Registry No. I, 1934-92-5; benzanilide, 93-98-1.

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Ruthenium-Catalyzed Cytochrome P-450 Type Oxidation of Tertiary Amines with Alkyl Hydroperoxides

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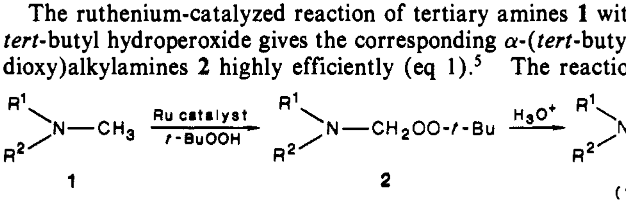
Oxidative N-dealkylation of amines is one of the important P-450 specific reactions,[1] and several model reactions using iron porphyrins have been reported.[2,3] During the course of our systematic studies on the simulation of enzymatic function of metabolism of amines with transition-metal catalysts,[4] we have found novel cytochrome P-450 type oxidation behavior with tertiary amines.

The ruthenium-catalyzed reaction of tertiary amines **1** with *tert*-butyl hydroperoxide gives the corresponding α-(*tert*-butyldioxy)alkylamines **2** highly efficiently (eq 1).[5] The reaction



$$R^1R^2N{-}CH_3 \ (\mathbf{1}) \xrightarrow[t\text{-BuOOH}]{\text{Ru catalyst}} R^1R^2N{-}CH_2OO{-}t{-}Bu \ (\mathbf{2}) \xrightarrow{H_3O^+} R^1R^2NH \quad (1)$$

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