K can also be separately calculated[6] by (6)

$$\frac{1}{(\phi_0/\phi)-1} = \frac{1}{K\tau} + \frac{K_r\tau'}{K\tau}[H_3O^+], \qquad (6)$$

where ϕ_0 is the fluorescene yield of cation when no proton transfer takes place and ϕ is the fluorescence yield of cation in more dilute acid solution. However, the rate constant calculated on this basis, works out to be an order of magnitude larger than calculated by lifetime measurements. This discrepancy cannot be attributed to the presence of various other anions like HSO_4^- or $HS_2O_7^-$. However, such anomalies are related to a 'configuration quenching' of the cation superimposed on the proton transfer reaction[7]. Those cations in the effective volume of which a water molecule or HSO_4^- ion is present at the moment of absorption, are supposed to transfer the proton immediately. Since this is assumed to be a very fast reaction, this will be reflected as a rapid decrease in the intensity measurements whereas the lifetime will remain unaffected resulting in a discrepancy in the two methods of calculation.

The neutral species has three modifications *viz.* quinonoid form, lactonic form and the ampho-ion. The lactonic form does not absorb in the visible or near ultraviolet and, therefore, does not contribute in the emission. The ampho-ion seems to be converted into the quinonoid form (4). The lactonic form is present mostly in organic non-ionic solvent but in aqueous solutions the dominant neutral form is the quinonoid form. It is not possible to determine the dissociation constant for the excited state in fluorescein cation because of the lactonic form occupying intermediate position between the cations and anions. However, taking into account the emission and absorption of the quinonoid form only, the excited state pK value of the cation was calculated for the quinonoid form by the Forster cycle

$$pK - pK^* = \frac{0.615}{T}(\nu_{FH^+} - \nu_F).$$

The value of pK^* comes out to be -1.3. The ground state pK being 2.2[2], the cation becomes more acidic in the excited state.

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SYNTHESIS OF α-METHYLARYLAMIDO-β-NAPHTHYL-(1-METHYLAMINO-2-METHYL-BENZIMIDAZOLYL)-ETHERS

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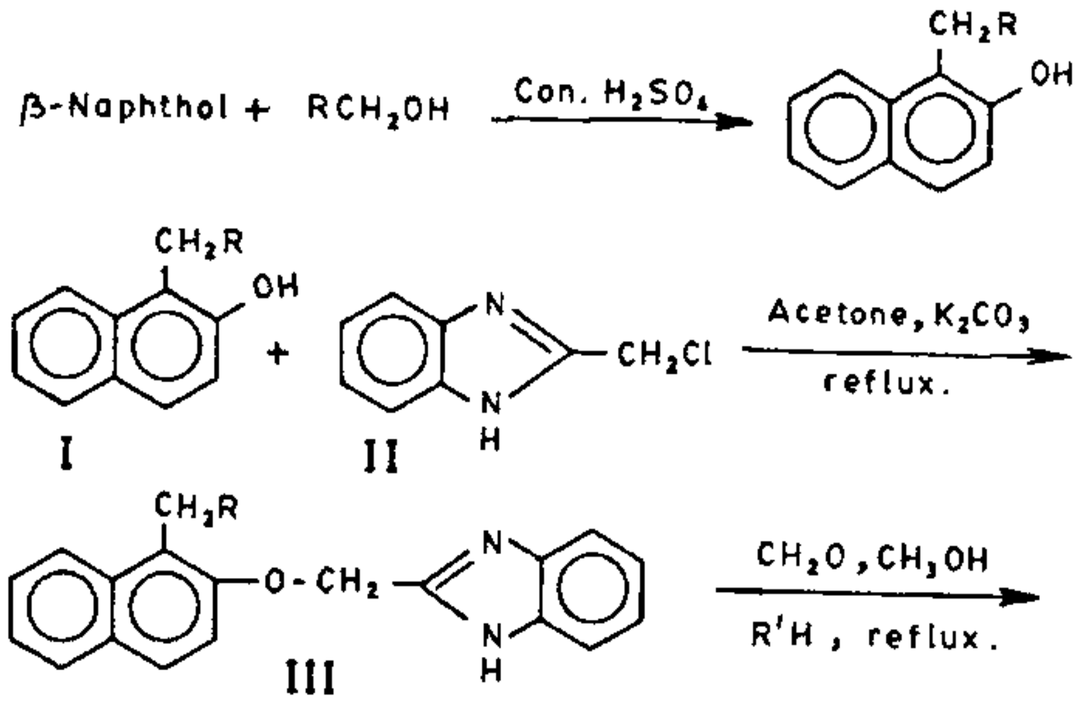
THE antifertility activity of various substituted ethers has been shown by many schools of research[1–4]. Tiwari and Subodh Kumar[5] reported the effectiveness of a few benzofuran derivatives containing ether linkage. It has been shown that these derivatives might get hydrolysed by enzymes in the human system to produce phenols which may act as biological carriers for the introduction of toxic residues for cellular metabolism[6,7]. In order to achieve more favourable therapeutic results, the authors synthesized a few ether derivatives containing benzimidazole nucleus.

N-hydroxymethylbenzamide, *N*-hydroxymethylphthalimide and *N*-hydroxymethylnicotinamide were condensed with β-naphthol in the presence of con. H_2SO_4 to yield α-methylarylamido-β-naphthol (I) which on condensation with 2-chloromethylbenzimidazole (II) gave α-methylarylamido-β-naphthyl benzimidazolyl-2-methyl ethers (III) in yields ranging from 40 to 50%. A mixture of III, formaldehyde solution and secondary amines on heating under reflux in methanol, afforded α-methylarylamido-β-naphthyl-(1-methylamino-2-methylbenzimidazolyl)-ethers (IV) in about 30% yields.

α-Methylarylamido-β-naphthols (*I*): *N*-hydroxymethylamides/imides were obtained following the procedure of Buc[8]. A mixture of β-naphthol (0.1 mol) and amidoalcohol (0.1 mol) was dissolved in minimum



R = Benzamido, Phthalimido or Nicotinamido.

R′ = Morpholino, Piperidino or N-Methylanilino.

quantity of conc. H_2SO_4 (15 ml). The reaction mixture was cooled and 20 ml of more conc. H_2SO_4 was added drop-wise with constant stirring and cooling and the reaction mixture was stirred for 1 hr at room temperature; the resultant reaction mixture was left overnight at room temperature, diluted with 200 ml of water, the solid product was filtered, washed with water to remove sulphonated product and recrystallised from dilute ethanol. The compounds, thus obtained, are listed in table 1.

α-Methylarylamido-β-naphthylbenzimidozolyl-2-methyl ethers (III): 2-Chloromethylbenzimidazole (II) was obtained following the procedure of King *et al*[9]. An equimolar quantity of α-methyl arylamido-β-naphthol and 2-chloromethyl benzimidazole (II) was dissolved in anhydrous acetone (30 ml) by warming. Anhydrous potassium carbonate (2 g) was added and the reaction mixture refluxed on a steam bath for 4 hr, cooled and filtered. The filtrate was concentrated. On cooling, a solid separated out which was filtered and recrystallized from ethanol. The ethers, thus obtained, are recorded in table 2.

Table 1 *α-Methylarylamido-β-naphthols (I)*

R-	M.P. °C	Molecular formula	Analysis nitrogen Calcd.	Found
Benzamido-	175	$C_{18}H_{15}NO_2$	5.05	5.15
Phthalimido-	175	$C_{19}H_{13}NO_3$	4.62	4.95
Nicotinamido-	115–116	$C_{17}H_{14}N_2O_2$	10.07	10.28

Table 2 *α-Methylarylamido-β-naphthylbenzimidazolyl-2-methylethers (III)*

R-	M.P. °(C)	Molecular formula	Analysis nitrogen Calcd.	Found
Benzamido-	100	$C_{26}H_{21}N_3O_2$	10.32	10.60
Phthalimido-	95	$C_{27}H_{19}N_3O_3$	9.69	9.48
Nicotinamido-	210	$C_{25}H_{20}N_4O_2$	13.72	13.97

α-Methylarylamido-β-naphthyl-(1-methylamino-2-methyl-benzimidazolyl)-ethers (IV): A mixture of α-methylarylamido-β-naphthylbenzimidazolyl-2-methyl ether (III) (0.001 mol), appropriate secondary amine (0.001 mol) and formaldehyde solution (40%) (0.0015 mol) in methanol (25 ml) was refluxed on a water bath for 2 hr. Excess of formalin and methanol was distilled off under reduced pressure. The pasty substance obtained was washed repeatedly with water and triturated with petroleum ether (b.p. 60–80°), dried and recrystallised from ethanol. The Mannich bases, thus synthesised, are presented in table 3.

Table 3 *α:Methylarylamido-β-naphthyl-(1-methylamino-2-methyl benzimidazolyl)-ethers (IV)*

R-	R′-	M.P. (°C)	Molecular formula	Analysis nitrogen Calcd.	Found
Benzamido-	Morpholino-	185	$C_{31}H_{30}N_4O_3$	11.06	11.23
Benzamido-	Piperidino-	190	$C_{32}H_{32}N_4O_2$	11.11	10.92
Benzamido-	*N*-Methylanilino-	175	$C_{34}H_{30}N_4O_2$	10.64	10.93
Phthalimido-	Morpholino-	245	$C_{32}H_{28}N_4O_4$	13.80	13.59
Phthalimido-	Piperidino-	235	$C_{33}H_{30}N_4O_3$	13.86	13.68
Phthalimido-	*N*-Methylanilino-	170	$C_{35}H_{28}N_4O_3$	13.28	13.47
Nicotinamido-	Morpholino-	255	$C_{30}H_{29}N_5O_3$	10.52	10.33
Nicotinamido-	Piperidino-	240	$C_{31}H_{31}N_5O_2$	10.56	10.77
Nicotinamido-	*N*-Methylanilino-	175	$C_{33}H_{29}N_5O_2$	10.14	10.38

The characteristic infrared spectral peaks at 1650 cm^{-1} (for > C = O in amide), 3350 cm^{-1} (for – NH of amide) and 1130 cm^{-1} and 1110 cm^{-1} (for a-cyclic ethers) further supported the formation of above compounds.

The antifertility activity of these compounds is in progress at CDRI, Lucknow and will be reported later.

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KINETICS AND MECHANISM OF THE BROMINATION OF AROMATIC SUBSTRATES BY N-BROMOSUCCINIMIDE IN AQUEOUS SOLUTION

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DESPITE the use of *N*-bromosuccinimide (NBS) as a brominating agent[1,2] since long, the mechanism of the reaction in aqueous medium is yet not clear. It is not clear whether NBS hydrolyses to form hypobromous acid, which then attacks the substrate or whether NBS directly attacks the substrate by halogen transfer. To elucidate this problem the kinetics of the rapid bromination of acetanilide and *m*-acetotoluidide as a typical case have been studied. To confirm the deductions, the kinetics of the bromination of the substrate by hypobromous acid (HOBr) have been studied under comparable conditions. As a further probe, the effect on the specific rate of potassium bromide and hydrochloric acid added to the NBS/HOBr has also been studied.

Since the reaction is too rapid for conventional techniques, it has been studied by the use of the rotating platinum electrode (RPE)[3-7]. It operates on the principle that at a potential of O.O V *vs* SCE applied at the RPE, only NBS or HOBr yields diffusion current proportional to its concentration, whereas neither the substrate nor the products of the reaction yield any diffusion current. Therefore the course of the reaction can be followed by monitoring the concentration of unreacted NBS from measurement of the diffusion current at intervals of time.

Analytical grade (BDH) chemicals were used to prepare stock solutions of various reactants and the latter were maintained in a thermostat at 25 ± 0.1°C. Equimolar solutions (4×10^{-4} M) of NBS and acetanilide containing 0.01 M potassium chloride as supporting electrolyte were rapidly mixed in a cell carrying the RPE and SCE and simultaneously a stop-watch was started. The diffusion current due to NBS at the RPE was measured with a mirror galvanometer with lamp and scale arrangement. The galvanometer deflections were earlier calibrated with NBS solutions of known concentration under identical experimental conditions. From these, the concentrations of unreacted NBS were determined at intervals of time. The experimental data fitted accurately into second order kinetic equation and a plot of 1/[NBS] *versus* time was satisfactorily linear. The slope of the curve evaluated by least square analysis was the specific rate (table 1). Repeated measurements of specific rates yielded results agreeing within ±3%.

Table 1 *Kinetics of bromination of acetanilide by N-bromosuccinimide in aqueous solution at 25.0°C*
Calibration of galvanometer deflection = 17.6 cm/10^{-4} M

Time/s	Diffusion current: galvanometer deflection/cm	Concentration of NBS unreacted [NBS]/10^{-4} M	1/[NBS] 10^3 M^{-1}
0	35.3	2.00	5.00
20	34.2	1.94	5.16
40	33.0	1.87	5.35
60	31.9	1.81	5.53
80	31.0	1.75	5.70
100	30.2	1.71	5.85
120	29.5	1.67	5.99
140	28.6	1.62	6.18
160	27.8	1.57	6.36
180	27.2	1.54	6.50
200	26.4	1.50	6.67
220	25.8	1.46	6.84
240	25.3	1.43	6.99

Slope of 1/[NBS] versus time curve = specific rate (k_2) = 8.5 M^{-1} s^{-1}