Photochemistry of Triethylamine–Acid Chloride Charge-transfer Complexes

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Charge-transfer (CT) complexes formed between various para-substituted benzoyl chlorides and triethylamine in acetonitrile have been studied spectrophotometrically. Photoactivation of these CT complexes lead to products arising from the reactions of acyl and aminoalkyl radicals. These photochemical processes have been utilized to generate acyl radicals from O-allylsalicylyl chloride which undergoes intramolecular cyclization to form 3-methylchroman-4-one 20 in good yields.

There is considerable interest in the development of new methods for generating acyl radicals, in view of their ability to undergo synthetically important inter- and intra-molecular carbon–carbon bond-forming reactions.[1–4] The reactions of acyl halides with organotin hydrides to form aldehydes have been proposed to occur via charge-transfer (CT) processes, involving the formation of acyl radicals.[5,6] Acyl halides are good electron acceptors and should be capable of forming CT complexes with electron-donor molecules. The present study was undertaken to examine the nature and photochemistry of the coloured complexes that are formed on addition of acid chlorides to tertiary amines in acetonitrile solutions. Photoactivation of these complexes led to products arising from aoyl and aminoalkyl radicals. The method of acyl radical generation using acid chloride–tertiary amine CT photochemistry was utilized to bring about the intramolecular cyclization of O-allylsalicylyl chloride to give the chromanone, 20. Chromanones are precursors to several series of biologically active compounds.

Results and Discussion

CT Complexes of Acid Chlorides with Tertiary Amines.—On mixing benzoyl chloride with triethylamine in dry acetonitrile, a yellowish-red colour develops. The corresponding changes in the absorption spectra are shown in Fig. 1. The broad absorption band (λ_{max} = 339 nm) is characteristic of CT transitions, associated with intramolecular donor–acceptor complexes. A less intense band also, associated with the complex is observed at ca. 420 nm. The formation constant, K (32.9 dm^3 mol^{-1}) as well as the extinction coefficient (368 dm^3 mol^{-1} cm^{-1}) at 339 nm, were determined spectrophotometrically by the Benesi–Hildebrand procedure for a 1:1 complex, using eqn. (1), under conditions where [Et$_3$N] $\gg$ [PhCOCl], A_{CT} is

$$\frac{[PhCOCl]}{A_{CT}} = \frac{1}{\varepsilon} + \frac{1}{\varepsilon K[Et_3N]} \quad (1)$$

the absorbance of the CT complex at 339 nm. The plot of [PhCOCl]/A_{CT} vs. 1/[Et$_3$N] is shown in the inset of Fig. 1. Addition of a large excess of triethylamine (> 35 fold), however led to a decrease in the CT band intensity. This may be attributed to the formation of the quaternary ammonium chloride (PhCON$^+$Et$_3$, Cl$^-$).

In non-polar solvents such as benzene, CT bands were not observed. Instead, a white precipitate of the quaternary ammonium salt was formed. This salt dissolves readily in polar solvents such as water and acetonitrile, yielding colourless solutions. Thus, it can be ruled out that the absorption bands in the visible region obtained on addition of acid chlorides to amines in acetonitrile are due to salt formation.
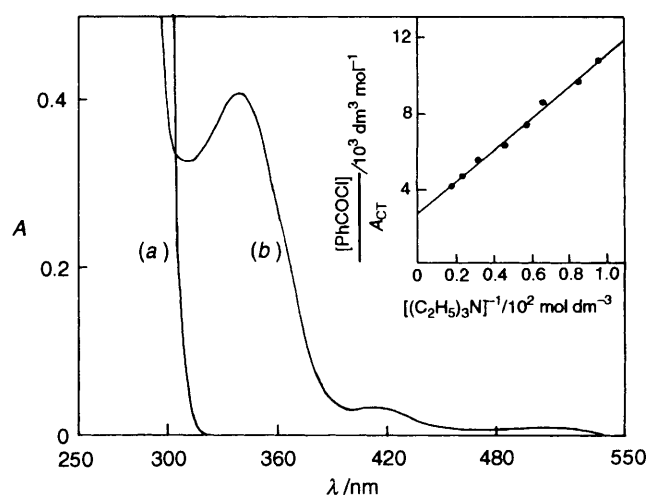

Fig. 1 CT absorption spectra of the complex of benzoyl chloride and triethylamine in acetonitrile. (a) Benzoyl chloride (1.7 × 10^{-3} mol dm^{-3}); (b) benzoyl chloride (1.7 × 10^{-3} mol dm^{-3}) and triethylamine (5.2 × 10^{-2} mol dm^{-3}). Inset shows plot of [PhCOCl]/A_{CT} vs. 1/Et$_3$N at 339 nm.

Table 1 Spectral characteristics, equilibrium constants of the CT complexes of triethylamine with various para-substituted benzoyl chlorides and the photochemical yield of the corresponding para-substituted amides

Acid chloride p-X-C$_6$H$_4$COCl	σ	λ_{max}/nm	ε/dm^3 mol^{-1} cm^{-1}	K/dm^3 mol^{-1}	Yield of amide (%)
X = OMe	−0.27	333	—	—	34
= Me	−0.17	338	285	13.8	31
= H	0.0	339	368	32.9	36
= Cl	0.23	342	161	37.2	50
= NO$_2$	0.78	346	—	—	12

The equilibrium constant and the spectral characteristics for the CT complexes formed by benzoyl chloride and para-substituted benzoyl chloride derivatives with triethylamine were determined and are presented in Table 1. The equilibrium constants for the formation of CT complexes of the p-methoxy and p-nitrobenzoyl chloride complexes could not be estimated accurately. In the former, formation of the quaternary salt and in the latter, the absorption spectrum of nitrobenzoyl chloride interfere with the measurements. The Hammett constant (σ) for the different substituents are also listed in Table 1. The increase in the λ_{max} of the CT band as well as the equilibrium constants with increasing values indicate that the presence of electron-withdrawing groups in the acceptor enhances the stability of the CT complexes formed.

CT Photochemistry of Acid Chloride–Triethylamine Complexes.—These CT complexes are thermally stable in solution and removal of the solvent gave the corresponding quaternary ammonium salts, in quantitative amounts. Selective irradiation of the long-wavelength CT bands, however leads to a rapid depletion of the bands. A solution of benzoyl chloride (552 mg, 3.93 mmol) and triethylamine (800 mg, 7.86 mmol) in acetonitrile (300 cm³) was irradiated with a Pyrex filtered light source for 5 h. Under these conditions, light is absorbed predominantly by the complex. After removal of the solvent under vacuum, the residue was washed with water, extracted with chloroform and analysed by gas chromatography, to indicate the formation of benzaldehyde (0.4%), benzil (0.2%), benzoic acid (41%) and N,N-diethylbenzamide (36%). Irradiation of solutions of the quaternary salt did not lead to any chemical changes.

Excitation of the CT complexes can lead to the formation of the acid chloride–triethylamine radical ion pair. A mechanism shown in Scheme 1, based on the known reactions of these

Scheme 1
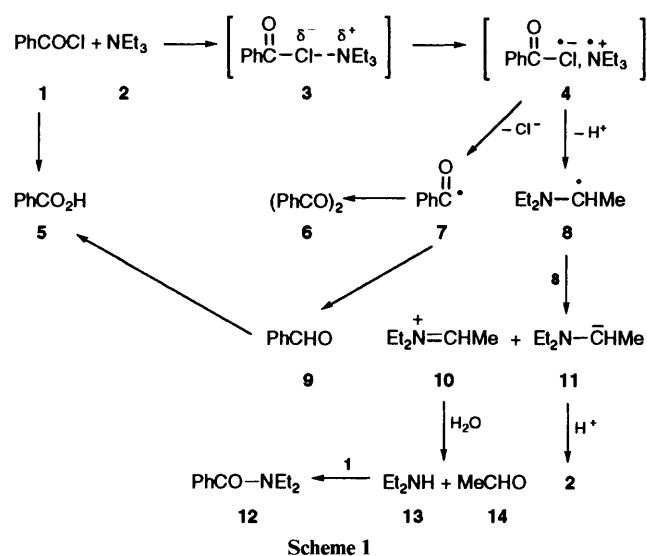
radical ions, has been proposed to explain the formation of the different photoproducts. The acid chloride radical anion **4** is known to be unstable[5–7] and can eliminate a chloride ion to yield the acyl radical **7**. The alkylamino radical cation that is also formed is known to be acidic relative to the parent amine[8,9] and can deprotonate to yield the α-aminoalkyl radical **8**. The process of radical ion dissociation may be facilitated by an intermolecular proton exchange between the radical ion pairs, as observed in the case of solvent caged ketyl and alkylamino radical ion pairs.[10–12]

Formation of benzil **6** can occur via the dimerization of **7**. Benzoyl radicals are known to efficiently abstract hydrogen atoms and hence can abstract the labile α-hydrogen from triethylamine to yield benzaldehyde **9**,[6,7] which can undergo facile air-oxidation to benzoic acid during work-up.[13] Some benzoic acid could also be formed by the hydrolysis of the unreacted benzoyl chloride, during work-up.

The α-aminoalkyl radical **8** that is formed is known to undergo disproportionation reactions to eventually yield a secondary amine **13**, and the parent amine as shown in Scheme 1.[8] During work-up the reaction of diethylamine and unreacted benzoyl chloride can lead to the observed benzamide **12**. Based on the stoichiometry of the proposed mechanism there should be a 1:1 relation between the yields of benzoic acid and **12**, which is indeed observed.

In order to estimate the photostability of the CT complexes of other para-substituted benzoyl chlorides with triethylamine,

the complexes were irradiated with Pyrex filtered light. For these systems only the yield of the amide photoproduct was monitored. These results are included in Table 1. Except for the p-nitro-substituted derivative, the efficiency of photoreaction increases with the increase in electron-withdrawing nature of the substituents. In the case of p-nitrobenzoyl chloride, its inherent absorption can interfere with the CT photochemistry.

CT Photochemistry of the O-Allylsalicylyl Chloride–Triethylamine Complex.—Since the CT photochemistry of acid chloride–amine complexes indicated efficient formation of acyl radicals, the utility of these reactions for carrying out intramolecular cyclization reactions has been investigated. Irradiation of acetonitrile solutions containing O-allylsalicylyl chloride **15** and triethylamine **2** in 1:1 and 1:2 ratios gave substantial yields of the intramolecularly cyclized product 3-methylchroman-4-one **20**, along with O-allylsalicylic acid **17** and N,N-diethyl-O-allylsalicylamide **18**. The formation of both the acid **17** and amide **18** in these reactions can be explained by a mechanism similar to that shown in Scheme 1, whereas the cyclized product **20** may arise through the cyclization of the acyl radical **16**, as shown in Scheme 2. Direct irradiation of

Scheme 2
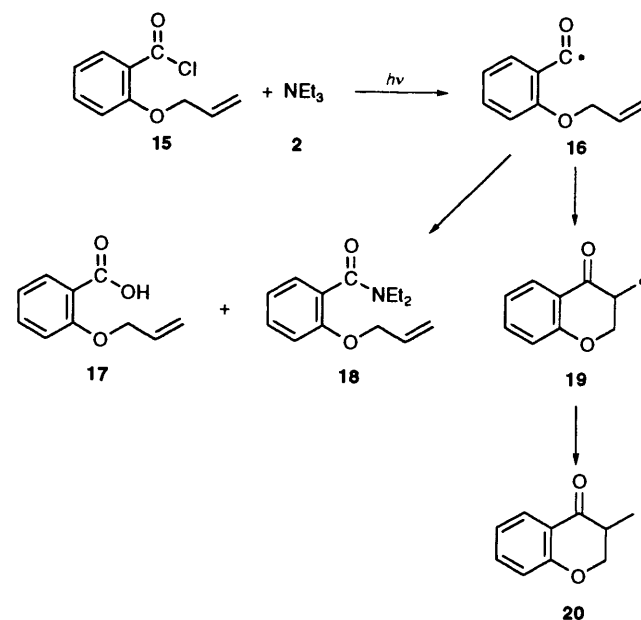
O-allylsalicylyl chloride **15** on the other hand resulted in the formation of only negligible amounts of the chromanone **20**.

Experimental

Commercially available acetonitrile used as solvent was distilled and stored over molecular sieves at least for 24 h prior to use. Acid chlorides were prepared by the reaction of the corresponding acids with thionyl chloride by standard procedures and were used after distillation. Triethylamine was purified by distillation over potassium hydroxide pellets. O-Allylsalicylic acid was prepared by refluxing methyl salicylate with allyl chloride in the presence of K_2CO_3 and 18-crown-6 in acetonitrile and subsequently hydrolysing the O-allyl ester formed.

UV spectra were recorded on a Shimadzu UV-2100 spectrophotometer. Irradiations were carried out in Pyrex tubes using a Hanovia 450 W medium pressure mercury lamp, which was kept cooled using a water-circulating jacket. A Rayonet photochemical reactor with 350 nm lamps was also used for irradiation. Gas chromatographic analyses were carried out

using a Hewlett–Packard model 5890 series II instrument, equipped with a flame ionization detector. Products were analysed using a 25 m × 0.2 mm × 0.3 μm capillary column (HP.FFAP) that uses TPA modified poly(ethylene glycol) as the stationary phase. The products were identified by comparing their gas chromatographic retention times with those of authentic samples and their mass spectra. Yields were estimated gas chromatographically using suitable internal standards. 3-Methylchroman-4-one **20** was characterized by its ^{1}H NMR, ^{13}C NMR and mass spectra.

NMR spectra were recorded on a JEOL JNM EX 90 (90 MHz ^{1}H, 22.5 MHz ^{13}C) NMR spectrometer in CDCl$_3$ solutions containing tetramethylsilane as internal standard. A Hewlett–Packard 5971 series mass selective detector was used to obtain the mass spectra.

Photolysis Experiments.—Photolysis of benzoyl chloride–triethylamine complexes. A mixture of benzoyl chloride (550 mg, 3.93 mmol) and triethylamine (800 mg, 1.1 cm^3, 7.86 mmol) in acetonitrile (300 cm^3) was irradiated using a Hanovia 450 W medium pressure mercury lamp for 5 h. After removal of the solvent under vacuum and washing the residual solid with water, the mixture was extracted with chloroform and analysed by GC. Benzaldehyde (1.5 mg, 0.4%), benzil (1.6 mg, 0.2%), benzoic acid (199 mg, 41%) and *N,N*-diethylbenzamide (248 mg, 36%) were detected as photoproducts.

Photolysis of para-substituted benzoyl chloride–triethylamine complexes. Mixtures of the appropriate *p*-substituted benzoyl chloride (3.93 mmol) and triethylamine (8 mmol) in acetonitrile (300 cm^3) were irradiated as in the earlier case. After work-up in the usual manner, the yields of the corresponding amides were estimated gas chromatographically and these are shown in Table 1.

Photolysis of O-allylsalicylyl chloride–triethylamine complex. A solution of *O*-allylsalicylyl chloride (214 mg, 1.08 mmol) and triethylamine (220 mg, 0.3 cm^3, 2.16 mmol) in acetonitrile (200 cm^3) was irradiated for 1.5 h in an RPR (350 nm lamp source). Work-up in the usual manner and analysis by GC indicated the formation of *O*-allylsalicylic acid **17** (14 mg, 7%) and *N,N*-diethyl-*O*-allylsalicylamide **18** (114 mg, 45%) and 3-methyl-chroman-4-one **20** (57 mg, 33%). The structure of **20** was confirmed through analytical and spectral data.[1,14]

Direct irradiation of *O*-allylsalicylyl chloride (225 mg, 1.14 mmol) in acetonitrile (200 cm^3) in a Rayonet Photochemical Reactor (350 nm lamp source) for 1.5 h in a blank run gave a small amount 3-methylchroman-4-one **20** (1 mg, 0.5%). *O*-Allyl salicylic acid **17** (70 mg, 34%) was isolated as the major product from these solutions.

Selected spectral data for **20**: δ_H(90 MHz; CDCl$_3$) 1.20 (3 H, d, *J* 9 Hz, CH$_3$), 2.65–3.05 (1 H, m, CH), 4.00–4.60 (2 H, m, CH$_2$), 6.90–8.00 (4 H, m, ArH); δ_C(22.5 MHz; CDCl$_3$) 10.35 (CH$_3$), 40.42 (CH), 71.90 (CH$_2$), 117.43, 120.29, 121.01, 127.00, 135.33, 161.46 (Ar), 194.31 (C=O); *m/z* 162 (M$^+$, 34%), 120 (100), 92 (49), 89 (4), 73.05 (4), 64.1 (13), 58.00 (4).

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