The Structure of Acyl Nitrates.

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Acyl nitrates show little or no tendency to react in the form $\mathrm{R{\cdot}CO^+NO_3^-}$. The possibility of a dual mode of ionisation is discussed.

In the search for other sources of acylium ions, it was decided to see if acyl nitrates ($\mathrm{R{\cdot}CO{\cdot}NO_3}$) would give any evidence of acylium-ion formation. It is well known that acyl nitrates behave as nitrating agents, and that they readily undergo thermal decomposition (Lachowicz, *Ber.*, 1884, **17**, 1281; 1885, **18**, 2990; Francis, *J.*, 1906, **89**, 1) to the corresponding acid anhydrides:

$$2\mathrm{R{\cdot}CO{\cdot}NO_3} \rightleftharpoons \mathrm{(R{\cdot}CO)_2O} + \mathrm{N_2O_5}$$

The nitrating action of these compounds has been attributed (Gold, Hughes, and Ingold, *J.*, 1950, 2467) to a small but stationary concentration of dinitrogen pentoxide. The small amount of dinitrogen pentoxide could conceivably arise by the acyl nitrate dissociating slightly in the two possible ways:

$$\mathrm{R{\cdot}CO{\cdot}O{\cdot}NO_2} \rightleftharpoons \mathrm{R{\cdot}CO^+} + \mathrm{NO_3^-}$$

and

$$\mathrm{R{\cdot}CO{\cdot}O{\cdot}NO_2} \rightleftharpoons \mathrm{R{\cdot}CO{\cdot}O^-} + \mathrm{NO_2^+}$$

the net result being:

$$2\mathrm{R{\cdot}CO{\cdot}O{\cdot}NO_2} \rightleftharpoons \mathrm{(R{\cdot}CO)_2O} + \mathrm{N_2O_5}$$

The previously reported unstable properties of benzoyl nitrate, prepared by Francis's method (*loc. cit.*) from powdered silver nitrate and benzoyl chloride at —20°, were confirmed. We have found, however, that the nitrate is more stable in solution, *e.g.*, in ether or methyl cyanide.

It was therefore decided to investigate a series of acyl nitrates prepared *in situ* from silver nitrate and acyl chloride, in an anhydrous solvent. The choice of solvent was largely governed by the low solubility of silver nitrate in most organic solvents and the desirability of using a solvent of high dielectric constant. Methyl cyanide ($\varepsilon \sim 39$) was finally selected. This method of preparation ensures that free hydrogen ion is not present (cf. Gold *et al.*, *loc. cit.*).

Solutions of benzoyl and *p*-methoxybenzoyl nitrate, kept at 0 to 5° for 2 hr., gave little indication of anhydride formation. 2 : 4 : 6-Trimethylbenzoyl nitrate gave small amounts of anhydride under these conditions, but the yields were not reproducible. Benzoic anhydride was not appreciably affected under the conditions used for the experiments.

It seemed that if these substances could exist in solution as acylium nitrates, $\mathrm{R{\cdot}CO^+NO_3^-}$, then the addition of an acid to such a solution might produce more of the corresponding anhydride:

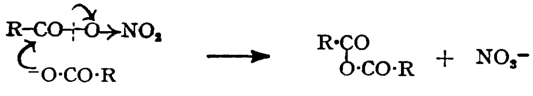
$$\mathrm{R{\cdot}CO^+NO_3^-} + \mathrm{R{\cdot}CO_2H} \rightleftharpoons \mathrm{(R{\cdot}CO)_2OH^+NO_3^-} \rightleftharpoons \mathrm{(R{\cdot}CO)_2O} + \mathrm{HNO_3}$$

This would be more feasible than the alternative reaction:

$$\mathrm{R{\cdot}CO_2^-NO_2^+} + \mathrm{R{\cdot}CO_2H} \rightleftharpoons \mathrm{(R{\cdot}CO)_2O} + \mathrm{HNO_3}$$

since here, the acid would have to supply an acylium ion to produce the anhydride.

It is also possible that separation of the nitrate ion from the acyl nitrate is assisted by the attack of, *e.g.*, the 2 : 4 : 6-trimethylbenzoate anion:



$$\underset{^{-}\mathrm{O{\cdot}CO{\cdot}R}}{\mathrm{R{-}CO{-}O{-}NO_2}} \longrightarrow \underset{\mathrm{O{\cdot}CO{\cdot}R}}{\mathrm{R{\cdot}CO}} + \mathrm{NO_3^-}$$

The overall reaction would again lead to the anhydride and nitric acid. A similar mechanism might well operate for the attack of an acyl nitrate molecule on another provided that some separation into the ions NO_2^+ and $R{\cdot}CO{\cdot}O^-$ occurred. In this case the products would be the anhydride and dinitrogen pentoxide.

Addition of acid, equivalent to 0·5 mole per mole of acyl nitrate, to the nitrate solutions generally gave only inconclusive evidence of anhydride formation. However, in the case of 2 : 4 : 6-trimethylbenzoic acid and the corresponding nitrate, 2 : 4 : 6-trimethylbenzoic anhydride was obtained in 80% yield, based on the amount of acid added. Some nitrated 2 : 4 : 6-trimethylbenzoic acid was also obtained. In the light of these experiments it seemed that more conclusive results might be obtained from the systems: 2 : 4 : 6-trimethylbenzoic acid–benzoyl nitrate and 2 : 4 : 6-trimethylbenzoyl nitrate–benzoic acid. In both these cases only small amounts of non-crystallisable products, which may have been mixed anhydride, were obtained. Synthetic mixtures of benzoic and 2 : 4 : 6-trimethylbenzoic anhydrides readily re-solidified after fusion.

Concurrently with these experiments, another series was investigated in which anisole was added to the acyl nitrate solution. Clearly, if any of the acyl nitrate reacted as the acylium compound, $R{\cdot}CO^+NO_3^-$, some ketone should be produced:

$$PhOMe + R{\cdot}CO^+ \longrightarrow R{\cdot}CO{\cdot}C_6H_4{\cdot}OMe + H^+$$

The possible production of *p*-methoxyacetophenone by interaction of anisole with the methyl cyanide, *i.e.*, the Hoesch reaction, was also kept in mind, but was considered a less likely alternative, under the conditions employed. In none of the cases investigated, *i.e.*, acetyl, benzoyl, *p*-nitrobenzoyl, or 2 : 4 : 6-trimethylbenzoyl nitrate, was any ketone produced. Only in the last case was any anhydride obtained. Nitroanisole was the only product isolated in all these cases, and this was predominantly the *ortho*-compound, as was observed by earlier workers (Griffiths, Walkey, and Watson, *J.*, 1934, 631).

It is clear from these experiments that there is little evidence for the formation of free acylium ions from acyl nitrates. This is in accord with the fact that nitrogen has less affinity than oxygen for the electrons of the O–N bond. In the case of the acyl nitrates, the polarisation of the carbonyl group would tend to make the nitrogen more positive.

Most of the nitrates investigated were stable under the conditions employed but the formation of small amounts of 2 : 4 : 6-trimethylbenzoic anhydride shows that 2 : 4 : 6-trimethylbenzoyl nitrate is rather less stable. This compound is clearly favourably constituted for ionisation as an aroyl nitrate, $Me_3C_6H_2{\rightarrow}CO^+{\rightarrow}NO_3^-$, since here the combined electron-repelling effects of the three methyl groups would aid the separation of the nitrate ion. The effect of adding 2 : 4 : 6-trimethylbenzoic acid clearly indicates that ionisation, as distinct from dissociation, may be occurring in this way.

While the failure to isolate acid anhydride from most of the nitration experiments does not exclude the possibility that the nitration involves dinitrogen pentoxide, there is a good indication that the aroyl nitrate itself might be the nitrating agent under these conditions.

EXPERIMENTAL

Experiments without Anisole.—Acid chloride (0·05 mole), dissolved in an equal weight of methyl cyanide, was added during 15 min. to a cooled solution of silver nitrate (0·05 mole) in methyl cyanide (17·0 g.). The addition was carried out at 0—5° with constant shaking and then the mixture was left at 0—5° for 2 hr., with occasional shaking. There was no marked tendency for the temperature to rise, but the mixture invariably developed a pale yellow colour on being kept. The precipitated silver chloride was filtered off so that the filtrate dropped directly on to crushed ice. The silver halide (94—96%) was washed with ether and with water. After separation of the ethereal layer, the aqueous liquor was extracted twice more with ether. The combined ethereal extracts were washed repeatedly with water or with aqueous sodium hydrogen carbonate. Owing to the relative stability of the acyl nitrates under these conditions, it was very difficult to remove all the nitrate by this procedure. The ethereal extracts often developed a marked acidity on standing. After evaporation of the dried (Na_2SO_4) ethereal solution, the residue was extracted with aqueous sodium hydrogen carbonate until free from acid and any residue was examined for anhydride.

In experiments where acid was also added, the appropriate compound (0·025 mole) was dissolved, together with the chloride, in a suitable quantity of methyl cyanide.

In most of these experiments the recovery of carboxylic acid was 88—94% of the theoretical amount.

2 : 4 : 6-*Trimethylbenzoyl Nitrate*.—This was prepared, as above, in the presence of 2 : 4 : 6-trimethylbenzoic acid (0·025 mole). The residue from the evaporation of the ethereal extracts was a waxy solid (6·4 g.) which crystallised readily from benzene–light petroleum as colourless flakes, m. p. 99—101°, which did not depress the m. p. of 2 : 4 : 6-trimethylbenzoic anhydride.

Acidification of the sodium hydrogen carbonate washings gave 6·0 g. of acid, which on extraction with light petroleum (b. p. 80—100°) gave some insoluble material (1·3 g.). The petroleum solution deposited crystalline material, m. p. 135°, that did not depress the m. p. of 2 : 4 : 6-trimethylbenzoic acid.

The sparingly soluble solid (later shown to be soluble to the extent of 1 part in 500 parts of boiling light petroleum, b. p. 80—100°) was recrystallised several times from light petroleum or benzene–light petroleum, and formed colourless prisms, m. p. 180°. A final crystallisation from aqueous ethyl alcohol gave material melting at 181° (Found: C, 57·7; H, 5·4; N, 6·6. Calc. for $C_{10}H_{11}O_4N$: C, 57·4; H, 5·3; N, 6·7%). Beringer and Sands (*J. Amer. Chem. Soc.*, 1953, **75**, 3319) give m. p. 180—182° for 2 : 4 : 6-trimethyl-3-nitrobenzoic acid.

2 : 4 : 6-*Trimethylbenzoic Anhydride*.—Dried sodium 2 : 4 : 6-trimethylbenzoate (4·5 g.) and 2 : 4 : 6-trimethylbenzoyl chloride (4·5 g.) in dry pyridine (35 ml.) were heated under reflux for 2 hr. The slightly impure anhydride (7·7 g.) was isolated by pouring the reaction mixture into ice-water. The brown solid crystallised from ethyl alcohol as colourless plates, m. p. 103—104° (Found: C, 77·0; H, 7·0. Calc. for $C_{20}H_{22}O_3$: C, 77·4; H, 7·0%). Fuson (*ibid.*, 1941, **63**, 2852) gives m. p. 106—107°.

Benzoyl Nitrate.—Freshly dried powdered silver nitrate (56 g.) in a flask fitted with a drying tube (P_2O_5), a dropping-funnel, and a thermometer, was shaken mechanically in an acetone–solid carbon dioxide bath. After being pre-cooled to −20°, benzoyl chloride (23 g.) was slowly added. Local overheating was unavoidable owing to the solidification of the benzoyl chloride and the general heterogeneous nature of the reaction mixture. The mixture was shaken at −17° to −13° for 2½ hr. Solid material was filtered off on a pre-cooled sintered filter and the filtrate was kept below −20°.

The nitrate was a pale yellow oil which hydrolysed readily with water. It decomposed on storage at room temperature with evolution of nitrogen dioxide; the residue gave some benzoic anhydride (m. p. and mixed m. p.).

Experiments with Anisole.—The anisole (0·1 mole) was added to the silver nitrate solution, prepared as above, before the addition of acid chloride. In these experiments there was often a marked tendency for the temperature to rise.

Results are collected in the following table.

R·COCl	Reaction time (min.)	Yield of nitroanisole (mole)
Acetyl	108	0·069
Acetyl + 0·2 mol. of Ac_2O	109	0·047
Benzoyl	135	0·064
p-Nitrobenzoyl	135	0·06
2 : 4 : 6-Trimethylbenzoyl	135	0·076

The fraction corresponding to nitroanisole in these experiments was collected at 128—132°/6 mm. (Found: N, 9·15. Calc. for $C_7H_7O_3N$: N, 9·15%).

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