Hydrolysis of Azoesters *via* Azoformate Intermediates

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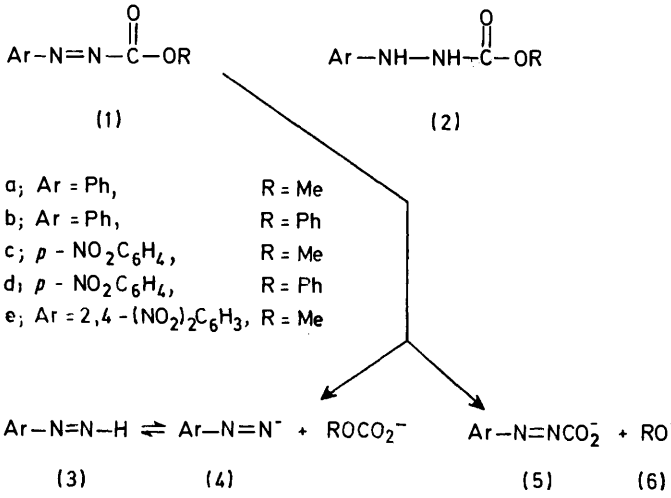
The alkyl- and aryl-azoformates (1) are hydrolysed in 4 : 1 water–dioxan solution at 25° by parallel acid, water, and base catalysed pathways. The initial products formed are the arylazoformates (5) which were detected spectrophotometrically and by their subsequent rates of (acid catalysed) decarboxylation. The azoesters (1) are highly reactive relative to benzoate esters (typically 10^4-fold for HO^- catalysis, 10^5-fold for H_2O reaction, and 165-fold for H_3O^+ catalysis) indicating strong electron withdrawal by the azo function is dominant relative to mesomeric electron release. Substituent effects in the aryl ring of (1) (ρ_{HO} 1.03, ρ_{H_2O} 0.88, $\rho_{H_3O^+}$ 0.44) indicate a 'transmission factor' of 0.54 for the −N=N− group. Decarboxylation of (5) is acid catalysed even at pH 10 and the carboxylate derived from the least basic azo-compound [5; Ar = 2,4-$(NO_2)_2C_6H_3$] shows an additional pH independent process at high pH, behaviour which is analogous to carbamates formed from weakly basic amines.

ALTHOUGH arylazoformic esters (1) have been known for a long time,[1,2] they have received, until recently,[3-6] little mechanistic attention. The main interest has centred on the use of the azo linkage for cycloaddition reactions [7-9] although oxidation (to azoxy compounds) [10] and reduction [to hydrazinoformates (2)] [11] are known. The



azoformates can also act as biological oxidising agents, as in the conversion of the tripeptide thiol, glutathione, to the corresponding disulphide (which induces diverse behavioural effects).[12,13]

The azoformates (1) can also undergo nucleophilic attack at the ester function. Hydrolysis can conceivably lead to either loss (from a tetrahedral intermediate) of the anions (6) or (4), depending on the leaving abilities of these two species. Anions (4) are known to undergo rapid loss of nitrogen and this route has been used by Hofmann [3,4,14] when Ar = *o*-halogenophenyl for benzyne syntheses. Monosubstituted azo-compounds (3) were not directly observed until 1965 by Kosower [6] although they had been proposed as intermediates in a variety of reactions including the oxidation of phenylhydrazines,[15] the Bamford–Stevens reaction,[16] the Wolff–Kishner reduction,[17] and the reductive deamination of aliphatic amines.[18]

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The alternative fragmentation of the ester yields an azoformate (5). These materials are known to be relatively stable in basic solution,[1] although rapid decomposition [probably also *via* the azo-compound (3)] occurs in acid. We have now examined in detail the hydrolytic pattern shown by these esters in order to determine their absolute reactivity (the activating effect of the −N=N− group), the effect of catalysis, and the balance between the various fragmentation routes, particularly when groups [Ar = 2,4-$(NO_2)_2C_6H_3$] which would favour direct breakdown to the anion (4) are present.

RESULTS AND DISCUSSION

The azoformates (1) were synthesised by lead tetra-acetate oxidation of the corresponding hydrazinoformates (2), a process which we have found to be satisfactory in all cases, contrary to literature [2] reports. The rates of hydrolysis of the esters (1) varied in a complex way with pH and subsequent rates and short-lived intermediates were observed at higher pH with esters (1a and b). An example of the latter behaviour is shown in Figure 1 where a repetitive scan of the u.v. spectrum of (1a) clearly indicates the build-up and decay of an inter-

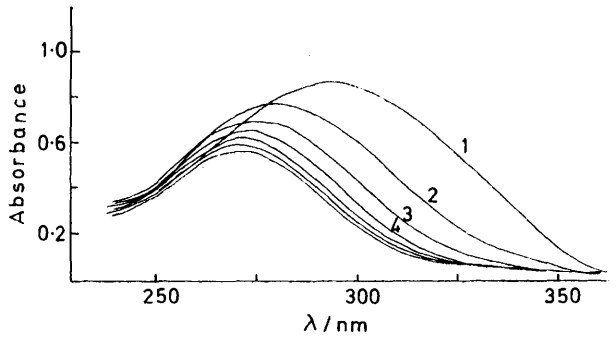


FIGURE 1 Repetitive scan of the u.v. spectrum of methyl phenylazoformate (1a) during hydrolysis at pH 9.55 in 4 : 1 water–dioxan at 25°. The interval between the scans is 2 min

mediate. The reaction is thus of the A→B→C type; however because of spectral characteristics of A—C it was possible to follow the rates of both processes independently. Thus the initial reaction (A→B) could be followed at 340 nm [where only the initial substrate A

(1a)] absorbs while the B→C process could be followed at 272 nm.

The results (see below) are consistent with the A→B process being the conversion of the ester (1) to the acid anion (5a), while C is the decomposition product from the diazene (3a). The observed rates (k_{obs}) of hydrolysis of (1a) (A→B) as a function of pH are summarised in Table 1. The reaction medium was 4 : 1 water–dioxan because of the low solubility of some of the substrates in pure water. A plot of log k_{obs} against pH (Figure 2) shows that hydrolysis of the ester is both acid and base catalysed and shows a large region (pH 2—6) where hydrolysis is pH independent. The rates of hydrolysis of the ester are correlated by equation (1) with the following values for the rate constants, k_{H_2O} 1.79×10^{-5} s^{-1}, k_{H^+} 1.39×10^{-4} l mol^{-1} s^{-1}, k_{HO^-} 3.16×10^{-2} l mol^{-1} these values have been used to construct the solid line (A→B) in Figure 2.

TABLE 1

Observed first-order rate constants for the hydrolysis of methyl phenylazoformate (1a)[a]

pH	$10^5 k_{obs.}$/s^{-1} [b]	$10^5 k_{obs.}$/s^{-1} [c]
0	16 [d]	
1.95	1.9 [d]	
3.82	1.9	
4.97	1.6	
7.01	6.05	
8.11	73	
8.52	135	
9.00	370	
9.50	950	
10.04	2 600	165 [d]
10.53	7 400	54 [d]
11.01		18 [d]
11.55		5.8 [d]

[a] In 4 : 1 water–dioxan (μ 1.0, NaCl) at 25°. [b] For hydrolysis of the ester (A→B). [c] For subsequent decarboxylation (B→C). [d] Measured at 300 nm; otherwise at 340 nm.

$$k_{obs.} = k_{H_2O} + k_{H^+}[H^+] + k_{HO^-}[HO^-] \quad (1)$$

The subsequent reaction (B→C) was followed over the pH range 10—11.6 and follows the simple acid catalysed

$$k_{obs.} = k'_{H^+}[H^+] + k_o \quad (2)$$

equation (2), with $k^1_{H^+}$ 2.0×10^7 l mol^{-1} s^{-1} and k_o 0. It was clearly shown by carrying out measurements at pH 10.5 that subsequent (rather than parallel) reactions were occurring; at this pH both the A→B and B→C processes (1) and (2) are summarised in Table 2. Only in the case of methyl 2,4-dinitrophenylazoformate (1e) does a pH independent rate of decarboxylation [equation (2), k_o 0] appear at high pH.

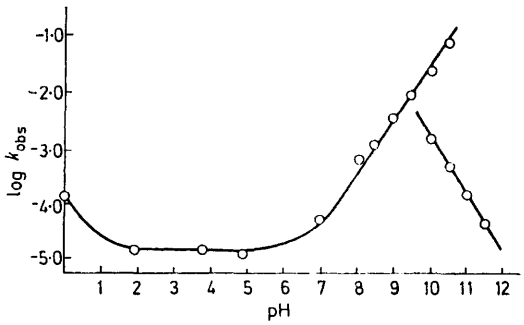


FIGURE 2 Plots of the log of the observed rate constants ($k_{obs.}$/s^{-1}) *versus* pH for the hydrolysis of methyl phenylazoformate (1a) (A→B) in 4 : 1 water–dioxan at 25° (μ 1.0, KCl), and for the subsequent decarboxylation of phenylazoformate (5a) (B→C). The lines are theoretical having been drawn using equations (1) (for A→B) and (2) (for B→C), respectively, with the values given for the constants in Table 2

In order to confirm that the B→C reactions were the decarboxylation of the azoformates (5), authentic samples of the latter were prepared from the methyl esters using the method of Kosower.[19] The anions (5; Ar = *p*-$NO_2C_6H_4$ and Ph) were relatively stable in 1 : 1 MeOH–H_2O at pH 13 (which was used as a stock solution) and portions of these were added to buffered solutions in the pH range 8—10. Plots of k_{obs} against pH showed specific acid catalysis and the average values obtained for k'_{H^+} were 1.0×10^6 l mol^{-1} s^{-1} for (5; Ar =

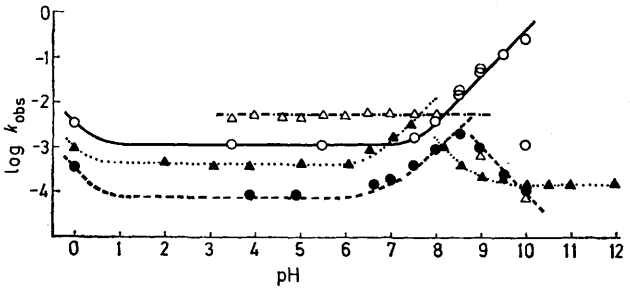


FIGURE 3 Plots of the log of the observed rate constants against pH (4 : 1 water–dioxan; 25°) for the hydrolysis of the following azoformates: (1b) (○); (1c) (●); (1d) (△); (1e) (▼). The rates of subsequent decarboxylation in the pH region of 8—12 are also shown. The lines are theoretical using the values of the constants listed in Table 2

TABLE 2

Summary of rate constants for hydrolysis of arylazoformates (1) and the decarboxylation of arylazoformic acids (5) formed *in situ* [a]

Substrate	Ester hydrolysis $10^4 k_{H^+}$/l mol^{-1} s^{-1}	$10^5 k_{H_2O}$/s^{-1}	$10^{-2} k_{HO^-}$/l mol^{-1} s^{-1}	$10^{-5} k'_{H^+}$/l mol^{-1} s^{-1}	Decarboxylation $10^4 k_o$/s^{-1}
(1a)	1.39	1.79	3.16		
(1b)	23.9	121	31.6	133	
(1c)	2.73	9.23	7.94	10	
(1d)		511			
(1e)	6.59	39.1	112	1.3	1.44

[a] In 4 : 1 water–dioxan (μ = 1.0 NaCl) at 25°.

(which vary in rate constant by >10-fold) can be measured separately with the same sample.

The kinetic data for the other esters are presented in Figure 3 and the derived rate constants to fit equations

p-$NO_2C_6H_4$) and 1.26×10^7 l mol^{-1} s^{-1} for (4; Ar = Ph), which compare favourably with the rate constants for the B→C reaction (see Table 2). Moreover the pH profiles for the decarboxylation of (5; Ar = Ph and p-$NO_2C_6H_4$) could be extended further to lower pH using this method than the *in situ* generation since at pH < 8.5 the decarboxylation step is faster than the initial ester hydrolysis.

Substituent Effects.—Since the observed rate constants were in general rather insensitive to substituent variation only gross changes [*e.g.* Ar = Ph→p-$NO_2C_6H_4$→2,4-$(NO_2)_2C_6H_4$] in the arylazo group were made. However even with these limited data it is possible to detect changes in the substituent response for the various reaction pathways. The Hammett ρ values obtained are listed, together with the catalytic species involved, in Table 3.

TABLE 3

Hammett ρ values for the hydrolysis of arylazoformate (1; R = Me)[a]

Catalyst	Hammett ρ value [b]
H_3O^+	0.44
H_2O	0.88
	0.80 [c]
HO^-	1.03

[a] In 4 : 1 water–dioxan at 25°. [b] A σ value of 0.78 was used for o-NO_2. [c] In this case R = Ph.

Since both aliphatic and aromatic leaving groups were used the results are best correlated in terms of Bronsted β (leaving group) values from plots of log k *versus* the pK_a of the conjugate acid of the leaving group using the available pK_a values of phenol (9.95) [20] and of methanol (15.09) [21] in water. The derived $\beta_{l.g.}$ values are summarised in Table 4.

Site of Cleavage.—With aliphatic azoformates either O–alkyl or O–acyl bond cleavage can conceivably occur while, if attack by the nucleophile is at the carbonyl group further reaction could give either N–C or C–O bond cleavage. While it is difficult to identify unequivocally the site of cleavage without the use of labelling studies, the evidence is in favour of acyl–oxygen bond breaking ($A_{AC}2$ and $B_{AC}2$ mechanisms as normally observed for esters). Thus reaction of esters (1) with methoxide [19] or ethoxide ion [3,14] gives the corresponding carbamates, while no dimethyl ether was observed among the products for the reaction of (1a) with methoxide ion. The correlation of the data for both aliphatic and aromatic esters also tends to support a similar mechanism for both series. Moreover the $\beta_{l.g.}$ values of Table 4 for HO^- catalysed hydrolysis are similar to that (−0.26) reported [22] for acetate esters known to hydrolyse by the $B_{AC}2$ mechanism. The spectrophotometric detection of azoformate anions (5) in all cases at pH > 8 indicates that at least under these conditions carbonyl–oxygen rather than carbonyl–azo bond fission is occurring.

Comparison with Benzoates.—The azoformates are highly activated relative to the corresponding benzoate esters. In Table 5 are listed the comparative rates of HO^- catalysed hydrolysis; the interpolation of the azo group typically enhances the rate of hydrolysis *ca.* 10^4-fold. This is surprising since an adjacent nitrogen in the *N*-methyl-*N*-(*p*-nitrophenyl)carbamate (7) actually reduces the reactivity of this ester *ca.* 3.5×10^4-fold relative to methyl *p*-nitrobenzoate or 4×10^6-fold relative to (1; Ar = p-$NO_2C_6H_4$, R = Me). Amide-type resonance stabilisation of the carbamate which is thought to be a major contributing factor to the lack of reactivity of (7) should also be present in the azoformate (1). Thus the azo-group has been shown to be a powerful electron donor when adjacent to an electron-deficient centre. An example of this is the stabilised carbenium ion (8) where the azo-group is powerfully electron donating; [24] other examples in which the linkage is overall electron donating are also known.[25] The azo-group is however overall electron withdrawing in (10) as shown by a pK_a of 11.3 [25,26] relative to 9.89 for (9).[27] In order to emphasise the resultant electron-withdrawing ability of the phenylazo-group in (1a), it can be calculated that a group would have to have effective σ value of 2.05 to

TABLE 4

Brönsted β values for the variation of the leaving group in the hydrolysis of the arylazoformates (1; Ar = Ph) [a]

Catalyst	Bronsted $\beta_{l.g.}$
H_3O^+	−0.31
H_2O	−0.36
	−0.34 [b]
HO^-	−0.21

[a] In 4 : 1 water–dioxan at 25°. [b] In this case Ar = p-$NO_2C_6H_4$.

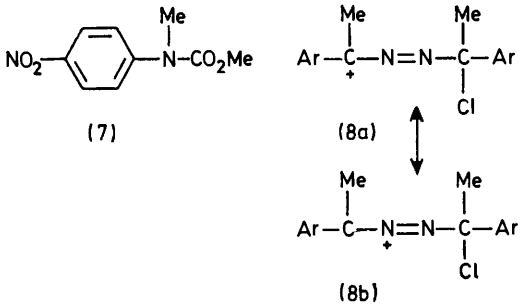


TABLE 5

Comparative rates of hydroxide catalysed hydrolysis of benzoate and azoformate esters

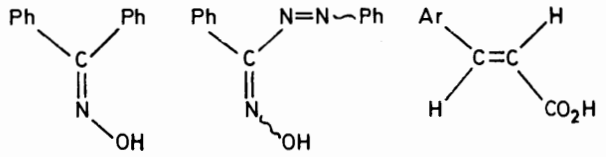
Benzoate	k_{HO^-}/l mol^{-1} s^{-1}	Azoformate	k_{HO^-}/l mol^{-1} s^{-1}	Ratio
$PhCO_2Me$ [a]	2.32×10^{-2}	PhN_2CO_2Me [b]	3.16×10^2	1.36×10^4
$PhCO_2Ph$ [c]	5.57×10^{-2}	PhN_2CO_2Ph [b]	3.16×10^3	5.7×10^4
p-$NO_2C_6H_4CO_2Me$ [a]	0.7	p-$NO_2C_6H_4N_2CO_2Me$ [b]	7.94×10^2	0.11×10^4

[a] In 33% dioxan at 25° (M. L. Bender and R. J. Thomas, *J. Amer. Chem. Soc.*, 1961, **83**, 4189). [b] In 4 : 1 water–dioxan at 25°. [c] In 33% acetonitrile (μ 0.3) at 25° (J. F. Kirsch, W. Clewell, and A. Simon, *J. Org. Chem.*, 1968, **33**, 127).

provide the same enhancement in the aryl ring of methyl phenylbenzoate. An extra factor enhancing the reactivity of (1a) may be steric facilitation (as observed with cinnamic acid esters) relative to benzoates.

Clearly from the data in Tables 3 and 5, the interpolation of of the azo group (which is *trans*) [8] reduces the sensitivity to substituent variation. The ρ value for substituent variation in hydroxide catalysed hydrolysis of methyl-substituted benzoates is +1.93 (in 33% dioxan at 25°),[28] so that the ρ value is reduced by 0.54-fold by the azo linkage in (1). This compares with a transmission factor of 0.47 for the *trans*-carbon–carbon double bond [from data for *trans*-cinnamic acids (11)].[29]

Neutral Hydrolysis.—Another interesting feature shown by the azo-esters (1) is the relatively rapid spontaneous (water catalysed) reaction (Figures 2 and 3); in contrast water catalysed hydrolysis is observed only in the case of highly activated benzoates and is then very slow. For example a value of 5.17×10^{-9} l mol^{-1} s^{-1} has been estimated [30] for the rate of reaction of water with *p*-nitrophenyl *p*-nitrobenzoate at 25° in 33% acetonitrile



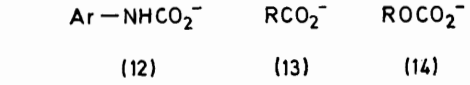
(9) (10) (11)

(indicating an enhancing factor of *ca.* 2×10^5-fold for the interpolation of the azo-group).

Water catalysed hydrolysis also shows a higher sensitivity to substituent variation in the arylazo group and in the leaving group than does hydroxide ion attack (see Tables 3 and 4). Because of the absence of data for H_2O attack on benzoates, it is not possible to make direct comparison; however greater sensitivity is generally observed in neighbouring group participation when a neutral nucleophile (relative to its conjugate base) is used. This has been attributed to rate-determining nucleophilic attack with the transition state being reached later on the reaction co-ordinate with the weaker nucleophile. An example is the cyclisation of *N*-acetylanthranilates for which ρ values (for leaving group variation) of 2.56 and 1.86 are reported for attack by the $NHCOCH_3$ and $NC(CH_3)O^-$ groups respectively.[31]

Acid Catalysed Hydrolysis.—Acid catalysis of hydrolysis of the azoformates (1) only becomes apparent in 1M-acid (see Figures 2 and 3) because of the importance of neutral hydrolysis. However hydrolysis is again enhanced relative to the corresponding benzoates (>165-fold from data for methyl benzoate).[32] The overall rate of acid catalysed hydrolysis is composite depending on the protonation equilibrium and the rate of water attack on the conjugate acid. Since the azo-group is more basic (as judged by the pK_a of −2.5 of azobenzene [33] relative to −7.36 for ethyl benzoate [34]), the larger fraction of protonated substrate present at a given acidity is probably a factor in the higher reactivity of (1). The ρ value for substituent variation in acid catalysed hydrolysis is close to zero,[35] due to cancellation of the effects for both steps. The small positive value (Table 3) observed for (1) is consistent with the substituent in Ar having a greater effect on the protonation equilibrium than on subsequent water attack.

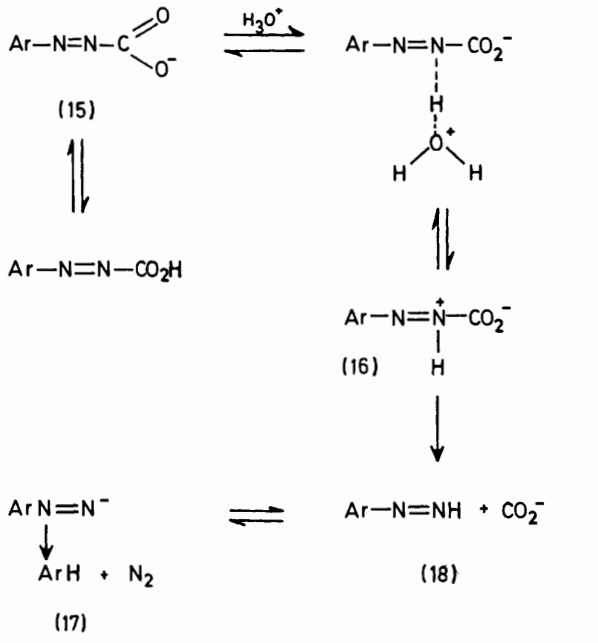
Decarboxylation of (5).—The decarboxylation of (5) is



(12) (13) (14)

mechanistically similar to the acid catalysed decarboxylation of *N*-arylcarbamates (12) which is also acid catalysed at low acidities. In fact the measured rate constants for the decarboxylation of the two series (5) and (12) (Ar = Ph or *p*-$NO_2C_6H_4$) do not differ by >5-fold. Moreover the azoformates (5) give similar ρ values [ρ −1.1 for (5), data from Table 2] compared with those which can be calculated (ρ −1.3) from data for carbamates (12) derived from weakly basic amines using data from Johnson [36] and Caplow.[37] It is therefore likely that a similar mechanism applies (Scheme) with rate-limiting carbon–nitrogen bond cleavage [(16)→(18)]. The azoate anion is unstable at high pH and reacts rapidly with loss of nitrogen to give in aqueous solution the hydrocarbon (17).

Figure 3 shows that at high pH decarboxylation of the



SCHEME

most weakly basic carboxylate [5; Ar = 2,4-$(NO_2)_2$-C_6H_3] becomes pH independent. This could be due to spontaneous decomposition of the carboxylate [5; Ar = 2,4-$(NO_2)_2C_6H_3$] due to stabilisation of the anion formed [2,4-$(NO_2)_2C_6H_3N_2^-$], or to a mechanism similar to that outlined in the Scheme with H_2O (rather than H_3O^+) acting as a general acid to protonate the substrate.

Both mechanisms have previously been observed for decarboxylations, *e.g.* spontaneous decarboxylation [38] for carboxylic acid anions (13), carbonates (14), and carbamates (12) derived from very weakly basic amines, while general acid catalysis is observed for carbamates derived from amines of intermediate basicity. It is clear therefore that the behaviour of the carboxylates (15) exactly parallels that of the corresponding carbamates. Moreover even the actual rate of the spontaneous decomposition of [15; Ar = 2,4-$(NO_2)_2C_6H_3$] is similar to that observed for the carbamate *N*-carboxyimidazolidone,[37] where the pK_a of the leaving groups involved are similar.

In conclusion, the hydrolysis of the azoformates studied is very rapid at 25°. All the esters studied react *via* azoformate intermediates which are detectable at high pH; there is no evidence, even when the best azo leaving groups are present, for direct azoate anion loss, rather than phenoxide loss, from the tetrahedral intermediate.

EXPERIMENTAL

Characterisation Methods.—M.p.s were measured on a Thomas Unimelt apparatus and are uncorrected. I.r. spectra were recorded on a Perkin-Elmer model 257 grating spectrophotometer. Solid samples were recorded in potassium bromide discs and liquid samples as thin films on rock salt plates. ^{1}H N.m.r. spectra were obtained on a Hitachi–Perkin-Elmer model R-20A spectrometer (operating at 60 MHz) with tetramethylsilane as an internal standard. Elemental analyses were performed by the Microanalytical Laboratory, University College, Cork.

Materials.—All inorganic materials used for kinetic measurements were AnalaR grade. Standard solutions of sodium hydroxide and hydrochloric acid were prepared by dilution of M and B Volucon ampoules with distilled water. Distilled water was obtained by twice distilling deionised water from alkaline potassium permanganate. The solvent used for the kinetic experiments, 4 : 1 water–dioxan, was prepared by mixing four volumes distilled water with one volume dioxan (B.D.H. AnalaR).

Substrates.—Methyl *N'*-(*p*-nitrophenyl)hydrazinoformate (2; Ar = *p*-$O_2NC_6H_4$, R = Me) was prepared by a method analogous to that used by Longo [2] in 61% yield, m.p. 179—181° (lit.,[4,39] 180°), $\bar{\nu}_{max.}$ (KBr disc) 3 350, 3 330 (NH), and 1 700 cm^{-1} (C=O), δ [$(CD_3)_2CO$] 3.68 (s, 3 H), 6.81—8.17 (q superimposed on s at 8.01, 5 H), 8.47br (s, 1 H).

Phenyl *N'*-(*p*-nitrophenyl)hydrazinoformate (2; Ar = *p*-$O_2NC_6H_4$, R = Ph) was prepared similarly from phenyl chloroformate and *p*-nitrophenylhydrazine in 36% yield except that the pyridine solution was diluted with absolute alcohol before it was added to the ice-cold 20% sulphuric acid solution. The ester was a light brown solid, m.p. 162—163° (from absolute alcohol), $\bar{\nu}_{max.}$ (KBr disc) 3 320 (NH) and 1 710 cm^{-1} (C=O), δ [$(CD_3)_2CO$] 6.94—8.21 (q and m).

Methyl *N'*-(2,4-dinitrophenyl)hydrazinoformate [2; Ar = 2,4-$(O_2N)_2C_6H_3$, R = Me]. The initial part of the preparation from methyl chloroformate and 2,4-dinitrophenylhydrazine (19.80 g, 0.10 mol) was similar to that of (2; Ar = *p*-$O_2NC_6H_4$, R = Me) [2] but a total of four equivalents of methyl chloroformate (37.80 g, 0.4 mol) had to be added before all the hydrazine reacted. T.l.c. (silica gel; benzene–acetone 20 : 1) of the solution after reaction showed two spots, R_F 0.14 and 0.20. The former was the more intense (under these conditions 2,4-dinitrophenylhydrazine had R_F 0.52). When the solution was added to ice-cold 20% sulphuric acid a red oil formed which solidified after 1.5 h. The solid was filtered and partly dissolved in hot ethanol (400 ml). On filtration, the filtrate was concentrated on a rotary evaporator and, after cooling in an ice–salt bath, gave methyl *N'*-(2,4-dinitrophenyl)hydrazinoformate [2; Ar = 2,4-$(O_2N)_2C_6H_3$, R = Me] as a yellow solid, (14.41 g, 56%) m.p. 135—139° (lit.,[2] 138°); $\bar{\nu}_{max.}$ (KBr disc) 3 362, 3 320 (NH), and 1 735 cm^{-1} (C=O).

Methyl *N'*-phenylhydrazinoformate (2; Ar = Ph, R = Me). A solution of methyl chloroformate (9.45 g, 0.1 mol) in dry ether (20 ml) was added dropwise to a stirred solution of phenylhydrazine (10.82 g, 0.1 mol) and dry triethylamine 10.1 g, 0.1 mol) in dry tetrahydrofuran (170 ml) in a three-neck round-bottom flask (250 ml), equipped with a condenser attached to a calcium chloride drying-tube, in an ice–salt bath. An insoluble adduct of methyl chloroformate and triethylamine formed. When the addition was complete the ice–salt mixture in the bath was replaced by hot water and the reaction mixture refluxed for *ca.* 30 min. Triethylamine hydrochloride was filtered off. The solvent was removed on a rotary evaporator to leave a yellow oil, which was dissolved in absolute ethanol. When a small amount of the ethanol solution was added to ice-cold 20% sulphuric acid a solid formed. The addition of this solid together with a small amount of the ice-cold 20% sulphuric acid solution to the ethanolic solution caused a solid to precipitate (8.7 g, 52%). Recrystallisation from water gave pure methyl *N'*-phenylhydrazinoformate (2; Ar = Ph, R = Me) (5.35 g, 32%), m.p. 114—115° (lit.,[2,8] 115—117, 115—116°), $\bar{\nu}_{max.}$ (KBr disc) 3 380, 3 215 (NH), and 1 725 cm^{-1} (C=O).

Phenyl *N'*-phenylhydrazinoformate (2; Ar = R = Ph) was similarly prepared from phenyl chloroformate and phenylhydrazine in 32% yield except that a second equivalent of phenylhydrazine was used instead of triethylamine, m.p. (from absolute ethanol) 118—121° (lit.,[8] 122—123°), $\bar{\nu}_{max.}$ (KBr disc) 3 318, 3 224 (NH), and 1 720 cm^{-1} (C=O).

Methyl phenylazoformate (1; Ar = Ph, R = Me) was prepared by the method of Kosower.[19] The *methyl ester* was obtained as a red oil which was distilled *in vacuo* under nitrogen, b.p. 77—80° at 3 mmHg (lit.,[19,39] 60—61° at 0.1 mmHg, 54° at 0.1 mmHg). (Found: C, 58.5; H, 5.25; N, 17.2. $C_8H_8N_2O_2$ requires C, 58.5; H, 4.9; N, 17.1%), $\bar{\nu}_{max.}$ (thin film) 1 760 cm^{-1} (C=O) (lit.,[19] in the range 1 754—1 773 cm^{-1} in $CHCl_3$), δ (CCl_4) 3.96 (s, 3 H), 7.3—7.95 (m, 5 H) [lit.,[7] δ (CCl_4) 3.94 (3 H) and 7.2—8.0 (5 H)].

The following compounds were similarly prepared: Phenyl phenylazoformate (1; Ar = R = Ph) as a red solid, m.p. 27—30° (lit.,[39] 29—30°), b.p. 150—158° at 0.25—1.0 mmHg, $\bar{\nu}_{max.}$ (thin film) 1 765 cm^{-1} (C=O), δ (CCl_4) 7.05—8.05 (m); methyl *p*-nitrophenylazoformate (1; Ar = *p*-$O_2NC_6H_4$, R = Me), an orange solid, 52%, m.p. 86—87° (from cyclohexane) (lit.,[2,19,39] 86.8—87.6, 85—87, 84—85°), $\bar{\nu}_{max.}$ (KBr disc) 1 760 cm^{-1} (C=O); phenyl *p*-nitrophenylazoformate (1; Ar = *p*-$O_2NC_6H_4$, R = Ph), an orange *solid* (89%), m.p. 118—120° (from cyclohexane) (Found: C, 57.5; H, 3.7; N, 15.1. $C_{13}H_9N_3O_4$ requires C, 57.6; H, 3.3; N, 15.5%), $\bar{\nu}_{max.}$ (KBr disc) 1 770 cm^{-1} (C=O).

Methyl 2,4-dinitrophenylazoformate [1; Ar = 2,4-$(O_2N)_2C_6H_3$, R = Me]. Londo [2] made an unsuccessful attempt to prepare this ester by oxidation of the corresponding

hydrazino-ester with dichromate. However, we have found that oxidation occurs when lead tetra-acetate is used as the oxidising agent. The *product* was an orange solid, m.p. 91—92° (from methanol) (Found: C, 38.7; N, 2.6; N, 21.3. $C_8H_6N_4O_6$ requires C, 37.8; H, 2.4; N, 22.0%), $\bar{\nu}_{max.}$ (KBr disc) 1 775 cm^{-1} (C=O), δ ($CDCl_3$) 4.03 (s, 3 H) and 7.38—8.73 (m, 3 H).

Kinetic Method.—The kinetics of hydrolysis of arylazoformates (1) were studied in 4 : 1 water–dioxan by following the change in optical density with time at 25° at suitable wavelengths using either a Perkin-Elmer PE 124 or Unicam SP 800 spectrophotometer. Both instruments were equipped with thermostatted multiple cell compartments and external recorders. Initial repetitive scans of the reaction solution in the u.v. region established suitable wavelengths at which an appreciable optical density change occurred during reaction. Kinetic runs were initiated by adding one or two drops of a solution of the substrate (10^{-2}M) in dioxan to a quartz cuvette containing a solution buffered at the required pH value, and previously equilibrated at 25° for 15 min. Mixing was achieved by shaking the solution. The change in optical density with time was then followed at a fixed wavelength. Pseudo-first-order rate constants were calculated from plots of log $(A_t - A_\infty)$ *versus* time, where A_t is the absorbance of the solution at any time t and A_∞ is the absorbance of the solution at time $= \infty$. In cases where the infinity 'drifted' the Guggenheim [40] method was used to calculate the rate constant, using data up to 95% reaction.

The pH of solutions outside the self-buffered regions (2 > pH > 12) was controlled by the use of acetate, phosphate, borax, and carbonate buffers (10^{-2}M). For cases other than 1M acid or base, sodium chloride was used to maintain the ionic strength at unity. Independent experiments showed that buffer catalysis at these concentrations was negligible. A Radiometer PHM 26 pH meter (with an expanded scale) and a Metrohm 125 U glass electrode was used for pH measurements. All 'pH' values quoted for the dioxan–water solutions are relative values measured directly for the solutions, no further corrections being applied. Prior to making pH measurements the pH meter was standardised with an appropriate Radiometer aqueous buffer solution (pH 4.01, 6.50, or 9.22 at 25°). The pH of the reaction solutions were measured before and after a kinetic experiment in order to check for pH drift. The same kinetic method was used for arylazoformic acids as for the arylazoformates except that more concentrated (5×10^{-2}M) buffer solutions were used to keep the pH constant; this was necessary since the stock solutions of the acids (prepared by dissolving the ester (10^{-4} mol) and sodium hydroxide (2×10^{-4} mol) in 1 : 1 methanol–water (10 ml)) were basic (*ca.* 10^{-1}M).

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