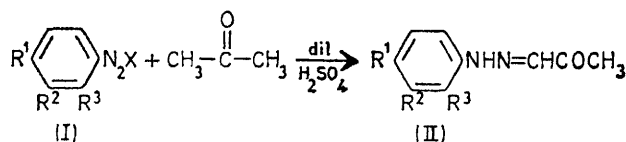


Coupling of Diazonium Salts with Acetone

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Diazonium salts or isodiazoates reacted with acetone in acid media to give the corresponding α -oxopropanal arylhydrazone in high yield. The kinetics of formation of α -oxopropanal *p*-nitrophenylhydrazone from sodium *p*-nitrobenzeneisodiazoate and acetone in presence of acids were studied in acetone solution at 25°. For a series of six acids of different acid strengths, pseudo-first-order rate constants were obtained, and the reaction was found to be of the second order, first order in the diazoate, and first order in acid. The mechanistic scheme proposed for hydrazone formation is supported by the present investigation.

CHATTAWAY *et al.*¹ found that when *o*-, *m*-, and *p*-nitrobenzenediazonium salts reacted with acetoacetic acid, coupling occurred and the corresponding α -oxopropanal arylhydrazone (IIa and c) was obtained. We now show that the hydrazones (IIa–j) could also be produced by



- | | |
|---|---|
| a; R ¹ = R ² = H, R ³ = NO ₂ | f; R ¹ = Br, R ² = R ³ = H |
| b; R ¹ = R ³ = H, R ² = NO ₂ | g; R ¹ = CO ₂ H, R ² = R ³ = H |
| c; R ¹ = NO ₂ , R ² = R ³ = H | h; R ¹ = CH ₃ , R ² = R ³ = H |
| d; R ¹ = R ³ = NO ₂ , R ² = H | i; R ¹ = OCH ₃ , R ² = R ³ = H |
| e; R ¹ = R ² = R ³ = H | j; R ¹ = SO ₃ Na, R ² = R ³ = H |

diazo-reaction of the corresponding diazonium salt (Ia–j) and acetone. The reaction is exceedingly slow in dilute aqueous solution, and more rapid in the presence of dilute sulphuric acid.

The i.r. spectra of the products showed absorption bands at 1680 cm⁻¹ (C=O str). There is also an absorption band at 1605 cm⁻¹ attributable to the conjugated C–N linkage.² Absorption at the N–H bending frequency appears in the range 1515–1540 cm⁻¹, and the absorption at 3280 cm⁻¹ (NH str) also established the presence of this linkage.^{2,3}

The isodiazoates from aniline, *p*-bromoaniline, and *p*-nitroaniline also coupled with acetone under acidic conditions to give (IIe, f, and c), respectively. Since acids convert isodiazoates into diazonium salts,⁴ they can be regarded as sources of diazonium salts. Because of the fact that the isodiazoate from *p*-nitroaniline was the only compound in this series that can be obtained entirely free from alkali,⁵ it was chosen for the kinetic studies.

The reaction of sodium *p*-nitrobenzeneisodiazoate with acetone was studied by spectrophotometric observation of the hydrazone (IIc) at 390 nm. No reaction was observed in dry acetone, and the reaction in 80% aqueous acetone was exceedingly slow, being more rapid in the presence of acids. Accordingly, the effects of acetic, formic, salicylic, oxalic, picric, and nitric acids on the reaction rate were examined at 25°. Reactions were carried out under pseudo-first-order conditions (at least a 100-fold excess of acid over the diazoate was

used throughout, and the reactant acetone which is required in large excess was also used as the solvent). Before the kinetic investigation, the reaction between the diazoate and acetone in the presence of the above mentioned acids was carried out to isolate the product. In every case, the product was α -oxopropanal *p*-nitrophenylhydrazone (IIc), identified by i.r. and u.v. spectra and by mixed m.p. with an authentic sample.¹ The rate of formation followed at 390 nm of the hydrazone (IIc) was thus assumed to be proportional to the concentration of the diazoate reacted. (No interference by acids, solvent, or diazoate was detected at 390 nm.)

RESULTS AND DISCUSSION

Reaction Rates.—The appearance of hydrazone was followed spectrophotometrically and satisfactory first-order rate constants were obtained for the reaction of the diazoate (DT) with acetone in six acids of varying acidity. The values did appear to be sensitive to the concentration and strength of the acid used. The concentration of acids ranged from 0.002 to 5M on going from nitric to acetic acid, and kinetic studies were carried out at four or five different concentrations for each acid, the initial diazoate concentrations being *ca.* 10⁻⁵M throughout (see Table I). The rate constants observed (*k*_{obs}) also showed a direct proportionality to the acid catalyst concentration (HA). The kinetic behaviour conformed accurately to the rate law (1); its integrated form gives equation (2)

$$-d[\text{DT}]/dt = k[\text{DT}][\text{HA}] \quad (1)$$

$$(2.3/t) \log ([\text{DT}]_0/[\text{DT}]_t) = k[\text{HA}] = k_{\text{obs}} \quad (2)$$

where subscripts 0 and *t* refer to zero time and time *t* respectively. Typical linear plots of log ([DT]₀/[DT]_{*t*}) versus *t*, in accord with equation (2), are depicted in Figure 1.

Table I records also the second-order rate constant as a function of acid concentration. The acid dependence of the reaction rates was studied for a series of runs using acetic, formic, salicylic, oxalic, picric, and nitric acids at fixed concentration of the diazoate (4.5 × 10⁻⁵M).

It can be seen from Table I, that for a variation of acid concentration over an order of magnitude the same rate constant *k* for each series of acids was obtained within experimental accuracy. Figure 2 illustrates the plots of *k*_{obs} versus [HA] which are linear within the error

² A. Weissberger, 'Chemical Applications of Spectroscopy,' Interscience, London, 3rd edn., ch. IV.

³ A. Albert, *J.C.S. Perkin I*, 1973, 1629, 1634.

⁴ H. H. Hodgson and E. Marsden, *J. Chem. Soc.*, 1945, 207.

⁵ M. Wojciechowski, *Roczniki Chem.*, 1934, 14, 739.

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¹ F. D. Chattaway and D. R. Ashworth, *J. Chem. Soc.*, 1933, 475.

of the data. The zero intercept of these linear plots is consistent with the fact that no reaction in the absence of acid catalyst could be detected.

Little is known of acid-base equilibria in aprotic solvents such as acetone⁶ so it is difficult to predict the magnitude of the acidity constants and therefore to correlate the rates of reaction with the dissociation constants of the six acids used in this investigation.

TABLE 1

Rate constants for the reaction of sodium *p*-nitrobenzenesulfonate with acetone in the presence of acids at 25°

[HA]/M	$10^5 k_{\text{obs}}/\text{s}^{-1}$	$10^5 k/\text{l mol}^{-1} \text{s}^{-1}$
HOAc		
1.00	1.31	1.31
2.50	3.25	1.30
3.50	4.49	1.30
5.00	6.48	1.30
HCO ₂ H		
1.00	5.00	5.00
1.50	7.37	4.91
2.50	12.17	4.90
3.00	14.86	4.95
<i>o</i> -HOC ₆ H ₄ CO ₂ H		
0.20	3.32	11.60
0.40	4.63	11.60
0.60	6.95	11.60
0.80	8.75	10.94
1.20	13.24	11.04
(CO ₂ H) ₂		
0.04	4.40	110.00
0.06	6.63	110.50
0.09	10.00	111.00
0.18	20.00	111.00
2,4,6-(NO ₂) ₃ C ₆ H ₂ OH		
0.0035	7.45	2 128.0
0.0070	15.20	2 717.0
0.0100	21.15	2 115.0
0.0150	32.63	2 173.0
HNO ₃		
0.002	5.87	2 935.0
0.003	8.70	2 900.0
0.004	11.60	2 900.0
0.006	17.45	2 908.0

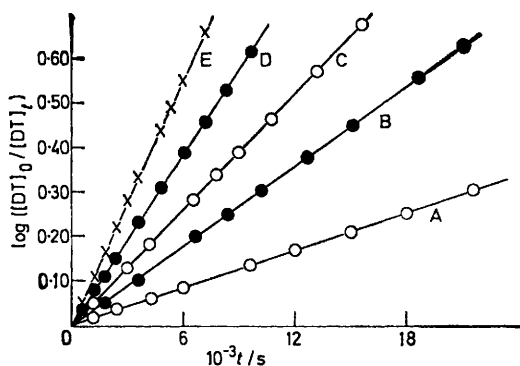


FIGURE 1 Representative pseudo-first-order rate plots according to equation (2). Reactions were carried out at constant initial concentrations of diazoate ($4.5 \times 10^{-6}\text{M}$) and variable concentrations of acids: A, 2.5M-HOAc; B, 0.6M-*o*-HOC₆H₄CO₂H; C, 0.09M-(CO₂H)₂; D, 3M-HCO₂H; E, 0.01M-2,4,6-(NO₂)₃C₆H₂OH

Dependence on Water.—The effect of water concentration for the reaction of sodium *p*-nitrobenzenesulfonate with acetone at constant acid concentration was

⁶ L. Meites, 'Handbook of Analytical Chemistry,' McGraw-Hill, New York, 1963.

examined. It appears that although the reaction is accelerated by the presence of water at fixed acid concentration; the log-log plots of (k_{obs}) versus water concentration shown in Figure 3 are not linear. The approximate value of 2 for each slope of the linear portions of

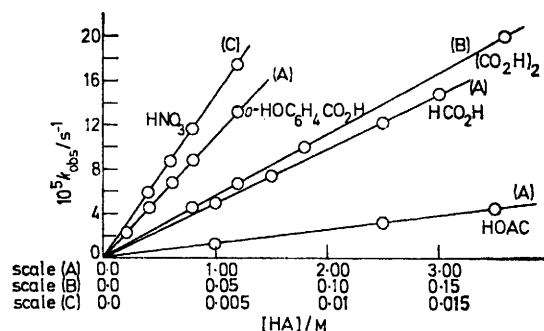


FIGURE 2 Effect of acid concentration on the reaction of sodium *p*-nitrobenzenesulfonate and acetone

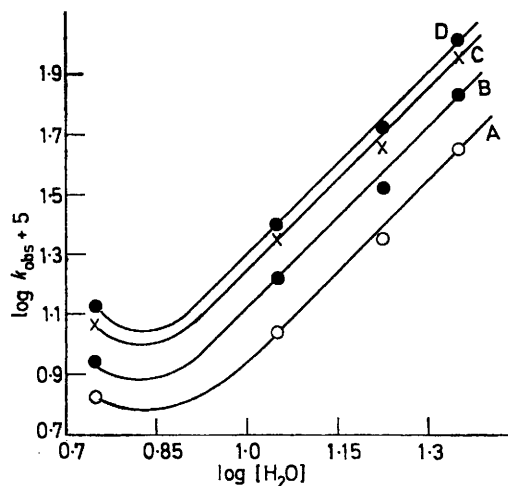


FIGURE 3 Effect of water concentration on the reaction of sodium *p*-nitrobenzenesulfonate and acetone in the presence of acids: A, 2.5M-HOAc; B, 1.0M-HCO₂H; C, 0.06M-(CO₂H)₂; D, 0.0035M-2,4,6-(NO₂)₃C₆H₂OH

the curves (Figure 3, plotted from data in Table 2) may indicate that the reaction has a second-order dependence on water concentration. Another possible explanation is that increasing concentration of water increases the polarity of the medium and permits further dissociation of the acid. It is worth noting from the data shown in Table 2, that the plots of $\log k_{\text{obs}}$ against the dielectric constant of the medium (Figure 4) are considerably more linear than the log-log plots of k_{obs} versus water concentration.

The rate constants for any acid in different media at constant temperature can be accurately represented by relation (3) where D is the dielectric constant of the

$$\log k = mD + n \quad (3)$$

acetone-water mixture and m and n are constants; m remains constant throughout. A constant value of 0.05 for m was obtained from the slopes of the linear plots of $\log k_{\text{obs}}$ versus D shown in Figure 4.

TABLE 2

Effect of water on the reaction rates between sodium *p*-nitrobenzenesulphate and acetone in various acids at 25°^a

[HA]	M	$\frac{[H_2O]}{g\ 100\ ml^{-1}}$	D^b	$10^5 k_{obs}/s^{-1c}$	m^d	n^d
2.5M-HOAc	5.6	10	24.0	5.76	0.05	-0.44
	11.2	20	29.6	10.95		
	16.8	30	35.7	22.26		
	22.4	40	41.8	44.91		
	5.6	10	24.0	7.80		
3.5M-HOAc	11.2	20	29.6	14.80	0.05	-0.31
	16.8	30	35.7	29.93		
	22.4	40	41.8	60.51		
	5.6	10	24.0	8.75		
	11.2	20	29.6	16.70		
1.0M-HCO ₂ H	16.8	30	35.7	33.30	0.05	-0.26
	22.4	40	41.8	67.90		
	5.6	10	24.0	7.98		
	11.2	20	29.6	15.20		
	16.8	30	35.7	30.60		
0.4M- <i>o</i> -HOC ₆ H ₄ CO ₂ H	22.4	40	41.8	61.90	0.05	-0.30
	5.6	10	24.0	11.80		
	11.2	20	29.6	22.58		
	16.8	30	35.7	45.00		
	22.4	40	41.8	91.58		
0.06M-(CO ₂ H) ₂	5.6	10	24.0	13.23	0.05	-0.13
	11.2	20	29.6	25.23		
	16.8	30	35.7	50.66		
	22.4	40	41.8	102.83		
	5.6	10	24.0	10.28		
0.0035M-2,4,6-(NO ₂) ₃ C ₆ H ₂ OH	11.2	20	29.6	19.22	0.05	-0.20
	16.8	30	35.7	40.00		
	22.4	40	41.8	79.80		
	5.6	10	24.0	24.0		
	11.2	20	29.6	29.6		

^a Concentration of diazoate $4.5 \times 10^{-5}M$. ^b Values of D were interpolated from ref. 7. ^c Average of at least two runs, rates were reproducible to $\pm 6\%$. ^d See equation (3).

It therefore appears that the second explanation is the correct one and that the reaction of sodium *p*-nitrobenzenesulphate with acetone is catalysed by acids and the observed first-order rate constants at constant acid

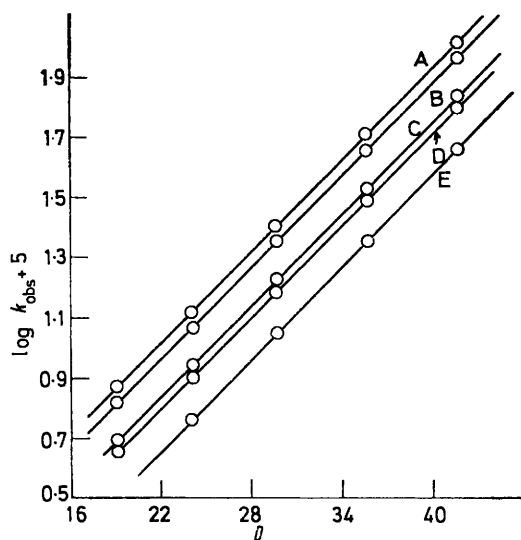
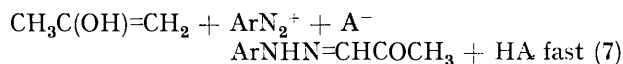
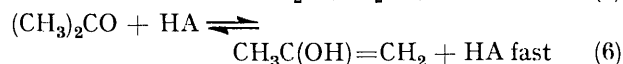
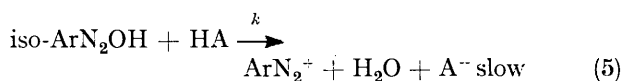
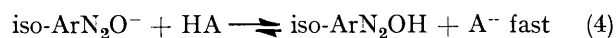


FIGURE 4 Dependence of $\log k$ on D for the reaction of sodium *p*-nitrobenzenesulphate and acetone in the presence of acids: A, 0.0035M-2,4,6-(NO₂)₃C₆H₂OH; B, 0.006M-(CO₂H)₂; C, 1.0M-HCO₂H; D, 0.4M-*o*-HOC₆H₄CO₂H; E, 2.5M-HOAc

concentration in the presence of water increase as the ionising power of the medium is increased.

Mechanism of Reaction.—The various experimental facts are insufficient to specify the reaction mechanism with much certainty, but the following scheme is com-

patible with the results. The isodiazote is first assumed



to be rapidly and stoichiometrically converted into the corresponding diazohydroxide which then undergoes a slow, acid-induced decomposition to the diazonium ion. This ion is then assumed to react rapidly with the enol form of acetone which will be present in a small constant concentration. There is no kinetic evidence for the involvement of the enol but we believe the reaction is most likely to proceed this way. The predicted rate equation for reactions (4)–(7) is (8), in agreement with experiment.

$$\frac{d[\text{Product}]}{dt} = k[\text{ArN}_2\text{OH}][\text{HA}] = k[\text{ArN}_2\text{O}^-][\text{HA}] \quad (8)$$

In the more aqueous mixtures the value of k will be expected to rise, again in agreement with the results.

EXPERIMENTAL

Materials.—The arylamines used in this investigation were purified by standard techniques. Glacial acetic acid for analysis (Feinchemie; Kallies) was dried with boron triacetate and distilled.⁸ Formic acid (B.D.H.; AnalaR; 98%;

⁷ G. Åkerlöf, *J. Amer. Chem. Soc.*, 1932, **54**, 4125.

⁸ W. C. Eichelberger and V. K. La Mer, *J. Amer. Chem. Soc.*, 1933, **55**, 3633.

d 1.22) was dried with boric anhydride and distilled under reduced pressure (12–18 mmHg) and 22–25°. Salicylic acid (AnalaR), m.p. 159°, was used. Oxalic acid was recrystallised from water and dehydrated at 100°. Picric acid (Eastman Kodak) was recrystallised from acetone and dried in a vacuum oven at 80° for 2 h. Nitric acid (B.D.H. AristaR; 70%) was distilled with an equal volume of sulphuric acid (*d* 1.84), redistilled over silver and barium nitrates, and fractionally distilled *in vacuo*.¹⁰ Acetone (Merck) was purified by shaking for 10 min with silver nitrate and sodium hydroxide solutions. It was filtered, dried (MgSO₄), and distilled.¹¹ Deionised water used in the kinetics was obtained by using an Elgastat deioniser (Elga).

Isodiazotates from aniline and *p*-bromoaniline were prepared by Schraube and Schmidt's method,¹² and were crystallised by dissolving in 95% ethanol at 40–50°, filtering, and precipitating carefully from ether.

added slowly and with stirring to a cold solution of acetone (60 ml) and sulphuric acid (12 ml; *d* 1.4). The mixture was kept for 1 h at 0–2° and for 4 h at room temperature, then diluted with water, and the precipitate was filtered off. The compounds isolated were identical with (IIe, f, and c) respectively.

Kinetic Measurements.—The rates of reaction were determined by spectrophotometric analysis for hydrazone using a Unicam SP 600 spectrophotometer. Reaction mixtures were made up in stoppered measuring flasks (100 ml) maintained at 25° in a thermostatted bath. Solutions of sodium *p*-nitrobenzenesodiazotate in dry acetone or in acetone–water mixtures were placed in the reaction flask and kept for 20 min to come to temperature. To start the reaction, the required acid previously weighed out into a short sample tube was dropped into the reaction flask and the flask was vigorously shaken until the contents were

TABLE 3
α-Oxopropanal arylhydrazones prepared from diazotised arylamines following procedure (a)

Compound	Yield (%)	M.p. (°C)	Crystallisation solvent	Found (%)			Formula	Required (%)			Ref.
				C	H	N		C	H	N	
(IIa)	87	128	EtOH				C ₉ H ₉ N ₂ O ₃				1
(IIb)	85	152	EtOH				C ₉ H ₉ N ₂ O ₃				1
(IIc)	93	217	EtOH				C ₉ H ₉ N ₂ O ₃				1
(IId)	90	172	EtOH	42.8	3.2	22.1	C ₉ H ₉ N ₂ O ₅	42.85	3.2	22.2	
(IIe)	90	149	C ₆ H ₆				C ₉ H ₁₀ N ₂ O				13
(IIf)	85	122	EtOH	44.9	3.65	11.6	C ₉ H ₉ BrN ₂ O	44.8	3.75	11.6	
(IIg)	90	212	EtOH	58.1	4.9	13.7	C ₁₀ H ₁₀ N ₂ O ₃	58.25	4.85	13.6	
(IIh)	83	84	HOAc–EtOH	68.2	6.8	16.0	C ₁₀ H ₁₂ N ₂ O	68.2	6.8	15.9	
(IIi)	80	91–92	HOAc–EtOH	62.5	6.2	14.5	C ₁₀ H ₁₂ N ₂ O ₂	62.5	6.25	14.6	
(IIj)	85	>300	EtOH–H ₂ O	40.7	3.4	10.7	C ₉ H ₉ N ₂ NaO ₄ S	40.9	3.4	10.6	

Sodium *p*-Nitrobenzenesodiazotate.—A 10% solution of *p*-nitrobenzenediazonium chloride, from *p*-nitroaniline (7 g), was poured rapidly into 18% aqueous sodium hydroxide solution (250 ml) at 50–60° with vigorous stirring. Golden yellow plates of the sodium salt separated on cooling, were recrystallised from 95% ethanol, and dried *in vacuo*.

Preparation of α-Oxopropanal Arylhydrazones.—(a) *From diazotised arylamines.* The method is exemplified by the preparation of α-oxopropanal *p*-nitrophenylhydrazone. A cold solution of diazotised *p*-nitroaniline [from *p*-nitroaniline, (7 g, 0.05 mol)] was buffered at pH 7 using a mixture of 0.1M-Na₂HPO₄ and 0.1M-KH₂PO₄. The solution was kept at 0–2° and divided into two equal parts. The first was added to a cold acetone (50 ml) and kept for 48 h at 0°; when diluted with water no product could be isolated. The second portion was added slowly to a cold mixture of acetone (50 ml) and sulphuric acid (5 ml; *d* 1.4). The mixture was kept for 1 h at 0–2° and for 4 h at room temperature. It was diluted with ice-cold water and the precipitate formed was filtered off. α-Oxopropanal *p*-nitrophenylhydrazone (4.8 g), bright yellow needles from 95% ethanol, had m.p. 217°, identical with that of an authentic sample.¹

The arylhydrazones listed in Table 3 were prepared similarly and crystallised from a suitable solvent.

(b) *From isodiazotates. General procedure.* The isodiazotates from aniline, *p*-bromoaniline, and *p*-nitroaniline (0.05 mol) were dissolved in ice-cold water (40 ml) and

homogenous. The operation requires <8 s. Samples of the reaction solution were withdrawn at suitable intervals and the optical density was determined at the absorption maximum for the hydrazone (λ_{max}, 390 nm). The reaction was followed until no further change in the optical density was apparent and the concentration of the hydrazone was calculated. In every case, this final optical density agreed to within ± 2% of the value expected for 100% reaction computed from the calibration curve of an authentic sample. All runs were arranged to be under pseudo-first-order conditions, and pseudo-first-order rates were obtained from the plots of log ([DT]₀/[DT]_t) against time. The rate constants reported are mean values of duplicate runs and are reproducible to within ± 6%. (Independent checks of the hydrazone stability in the presence of acids were made.)

Concentration Ranges.—The minimum concentration (*ca.* 2.3 × 10⁻³M) of the diazoate was fixed by the need for a change of optical density of *ca.* 0.6 in the 1 cm cell. Acetone which was required to be in large excess was used as solvent. The maximum concentration of acids was fixed by the maximum rate which could conveniently be measured. In all cases at least a 100-fold excess was used.

I.r. spectra were determined with a Unicam SP 200 spectrophotometer (KBr discs).

[3/2450 Received, 29th November, 1973]

⁹ H. I. Schlesinger and A. W. Martin, *J. Amer. Chem. Soc.*, 1914, **36**, 1589.

¹⁰ V. H. Veley and J. J. Manley, *Chem. and Ind.*, 1903, 1227.

¹¹ E. A. Werner, *Analyst*, 1933, **58**, 335; A. Weissberger and E. S. Proschkauer, 'Organic Solvents,' Interscience, New York, 1955, 2nd edn., ch. V.

¹² C. Schraube and C. Schmidt, *Ber.*, 1894, **27**, 514.

¹³ P. R. Japp and F. Klingemann, *Annalen*, 1888, **247**, 217.