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Mechanism of Benzidine and Semidine Rearrangements. Part XX.¹ Kinetics and Products of the Acid Conversions of 2,2'-Dichloro-, 4-Chloro-, and 4,4'-Dichloro-hydrazobenzene

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In '60%' aqueous dioxan at 0° the acid conversion of 2,2'-dichlorohydrazobenzene is much slower than that of the difluoro-analogue but has the same kinetic form : it is of first order in hydrazo-compound and second order in hydrogen ions. Independently of the acidity, this conversion leads to 94% of the corresponding benzidine and 6% of the products of disproportionation. The acid conversion of 4-chlorohydrazobenzene in similar conditions has an identical kinetic form. Independently of the acidity, it gives 19% of the corresponding diphenyline, 30% of the o-semidine, 20% of the p-semidine, and 31% of the products of disproportionation. The acid conversion of 4,4'-dichlorohydrazobenzene also has the same kinetic form. Independently of the acidity, it produces 22% of the o-semidine and 75% of the products of disproportionation. These findings lead to the conclusion that each of the simultaneous reactions of these hydrazo-conversions, whether it leads to a benzidine, a diphenyline, an o-semidine, a p-semidine, or products of disproportionation, has individual kinetics of the same form, viz. of first order in hydrazo-compound and second order in hydrogen ion.

THIS is a paper of mixed subjects; for the three hydrazobenzenes with which we shall be concerned provide different main points of interest. Following up the study in the preceding paper of the acid conversion of 2,2'-difluorohydrazobenzene, that of 2,2'-dichlorohydrazobenzene constitutes the next step in a progression somewhere along which, according to the polar-transition-state theory, one might encounter a change of mechanism. Again, according to this theory, the corresponding progressions involving 4-halogeno-hydrazobenzenes and 4,4'-dihalogenohydrazobenzenes should not show this phenomenon; so that, from this point of view, their study has the status of control experiments. Our more positive interest in the acid conversion of 4-chlorohydrazobenzene relates, first, to p-semidine formation, of which it is an important example, and secondly, to the kinetics of disproportionation. 4,4'-Dichlorohydrazobenzene provides a further example for study of the last-named subject.

Acid Conversion of 2,2'-Dichlorohydrazobenzene

Kinetics.-The acid conversion of 2,2'-dichlorohydrazobenzene in '60%' aqueous dioxan is very slow, 10^2 -times slower than that of 2,2'-difluorohydrazobenzene at like temperatures. The present study was at 0° , where, with 0.8N-perchloric acid as catalyst, the half-life was about 3 weeks, though on increasing the concentration of perchloric acid to 2.8N the rate was increased by a factor of more than 20,000.

We employed perchloric acid to provide acidities up to 2.8 N. Such acidities are far above the range of those for which Hammett's function h_0 in '60%' aqueous dioxan parallels hydrogen-ion concentration. Knowing, as we do, that all catalytic protons (both when there are two) which are involved in benzidine rearrangements, are added in pre-equilibria, no simple relation between rate and hydrogen-ion concentration is to be expected; and none is found. We have to interpret the kinetics with the aid of an h_0 function appropriate to the solvent and its salt content.

¹ Part XIX, D. V. Banthorpe and M. O'Sullivan, preceding paper.

These conditions prescribed a form of organisation of kinetic runs suitable to the available h_0 scales. We had two useful acidity scales for perchloric acid in ' 60% ' aqueous dioxan. One was one of those recorded in Part VIII² for perchloric acid with lithium perchlorate in this medium at certain constant ionic strengths, including $\mu = 1.0$. This scale could take care of acid concentrations up to 1.0N; and kinetic runs could be conducted up to this limit of acidity at the constant ionic strength $\mu = 1.0$, so avoiding variation in ionic-strength effects with varying acidity. For acid concentrations from 1.0 to 2.8N, we had available the acidity scale, developed by Bunton, Ley, Rhind-Tutt, and Vernon, for salt-free perchloric acid in ' 60% ' aqueous dioxan.³ The kinetic runs with which this scale was to be used had to be done without added salt, the ionic strength being allowed to go up with the acidity from run to run. However, because ionic-strength effects on rate become much less drastic towards these higher ionic strengths (probably because of the second Debye-Hückel term), we hoped to avoid excessive trouble from this partial neglect of salt effects. The making-up of ionic strengths with lithium perchlorate to much higher values than $\mu = 1$ would in any case have been rendered difficult by the tendency of lithium perchlorate in high concentration to salt-out the organic solutes.

All runs accurately obeyed the first-order law. This showed that the overall acid conversion of 2,2'-dichlorohydrazobenzene, nearly all of which results in rearrangement to the isomeric benzidine, is kinetically of first order in the hydrazo-compound.

Data showing the dependence of the first-order rateconstants on the acid concentration and on the acidity functions mentioned are given in Table 1. A plot of the logarithm of the rate constant against $H_0 = -\log h_0$ is shown in Figure 1. The line drawn has a slope of 2.00. We conclude that, like the acid conversion of hydrazobenzene, and of 2,2'-difluorohydrazobenzene, that of

² D. V. Banthorpe, E. D. Hughes, C. K. Ingold, and J. Roy,

J. Chem. Soc., 1962, 3294. ³ C. A. Bunton, J. B. Ley, A. J. Rhind-Tutt, and C. A. Vernon, J. Chem. Soc., 1957, 2327.

2,2'-dichlorohydrazobenzene 1s of second order in hydrogen ions.

For concentrations up to 2N-perchloric acid, the mean third-order rate-constant k_3 is 0.034×10^{-3} sec.⁻¹ mole⁻² 1.² in the '60% ' solvent at 0°. The corresponding

TABLE 1

Dependence of first-order rate constant $(k_1 \text{ in sec.}^{-1})$ of the acid conversion of 2,2'-dichlorohydrazobenzene on the concentration and acidity function of perchloric acid at ionic strength 1.0 and above and at 0°. (Initial concentration of hydrazo-compound about 0.004M)

HClO ₄	LiClO ₄	H_0	$10^{5}k_{1}$	10 ³ k ₃
0.80	0.20	0.87	0.061	0.034
1.00	0.00	0.75	0.107	0.034
1.60	0.00	0.10	1.93	0.031
2.00	0.00	-0.56	13.1	0.039
2.84	0.00	-0.99	1470	(0.154)

two-proton rate constant for hydrazobenzene² is 1580×10^{-3} sec.⁻¹ mole⁻² l.². The two 2-chloro-substituents therefore reduce the rate of conversion by a



FIGURE 1 Plot of the logarithm of the first-order rate constant of conversion of 2,2'-dichlorohydrazobenzene against H_0 for perchloric acid in '60% 'aqueous dioxan at 0°, and ionic strength equal to 1.0 or to the acid concentration when higher. The line has slope 2.00

factor of 46000 (at 0°). In Part XIX¹ it was computed that two 2-fluoro-substituents reduced the rate of twoproton conversion by a factor of 640 (at 25°). The a-halogens are thus deactivating in the order Cl > F.

We attribute the lower rate of the two-proton reaction of 2,2'-dichlorohydrazobenzene than of 2,2'-difluorohydrazobenzene partly to the greater base-weakening effect of the larger *ortho*-halogen substituent, but mainly to the cutting back in the latter of the electropositive conjugation characterising the electromeric effect of halogens in electron-demanding reactions, by the larger size of the valency shell of chlorine than of aromatic carbon, and the consequent impairment of orbital overlap. **Products.**—As is commonly the case in acid conversions of 2,2'-disubstituted hydrazobenzenes, 2,2'-dichlorohydrazobenzene gave only one rearrangement product, a benzidine, and this accounted for nearly the whole of the material. The identification of the main product as $3\cdot3'$ -dichlorohydrazobenzene had already been accomplished by Cohn,⁴ who prepared it for comparison by the known independent method from NN'-diacetylbenzidine by chlorination and subsequent deacetylation.⁵ As recorded in Table 2, our chromatograms on formamide–ethanol paper developed with cyclohexane disclosed nothing other than this mainproduct and the two products of disproportionation, 2,2'-dichloroazobenzene and 2-chloroaniline.

TABLE 2

Products from the acid conversion of 2,2'dichlorohydrazobenzene

	3,3'-Dichloro- benzidine	2,2'-Dichloro- azobenzene	2-Chloro- aniline
$R_{\rm F}$ (cyclohexane)	0.53	1.00	0.89
Colour 1 *	Orange	Orange †	Yellow
Colour $2a * \dots$ Colour $2b * \dots$ Abundance \dots	$\begin{array}{c} \text{Mauve} \\ 94\% \end{array}$	3%	$\mathrm{Purple}\ \mathbf{2 imes3}\ \mathrm{mol.}\ \%$

* Colour 1 was obtained with p-dimethylaminobenzaldehyde, colour 2*a* with nitrous acid, and colour 2*b* by following the nitrous acid by treatment with *N*-1-naphthylethylenediamine dihydrochloride. \dagger Original colour.

Quantitative estimates were made spectrophotometrically of the products formed in 1.0N- and in 2.8N-acid. The results were identical and were as given in Table 2. The ratio of disproportionation to rearrangement is evidently independent of the acidity, and thus both processes must have the same kinetic order in hydrogen ions. This is therefore a two-proton disproportionation.

Acid Conversion of 4-Chlorohydrazobenzene

Kinetics.—The rate of this acid conversion is about $10^{3\cdot5}$ -times greater than that of 2,2'-dichlorohydrazobenzene. The conversion of 4-chlorohydrazobenzene was studied kinetically in '60%' aqueous dioxan at 0° with acidities provided by perchloric acid in the concentration range 0.07—1.00N. The ionic strength was made up to 1.00 by additions of lithium perchlorate throughout the main series of runs. The acidity scale providing h_0 values appropriate to these conditions is given in Part VIII.²

All runs have good first-order rate constants, so showing that the kinetic order in hydrazo-compound of the overall conversion is unity. As we shall see, quite a large fraction of this conversion leads to disproportionation, and therefore the kinetic order in hydrazocompound of rearrangement and disproportionation must each be unity.

A comparison of the first-order rate constants with the acid concentration and the acidity function, $H_0 =$

⁵ Levinstein Ltd. Patent, cf. Chem. Zentr., 1898, I, 295.

⁴ P. Cohn, Ber., 1900, 33, 3552.

 $-\log h_0$, appropriate to the medium is given for the runs of Series 1 in Table 3.

TABLE 3

Dependence of the first-order rate constant $(k_1 \text{ in sec.}^{-1})$ of conversion of 4-chlorohydrazobenzene on the concentration and acidity function of perchloric acid in '60%' aqueous dioxan at 0° (Initial concentration of hydrazo-compound about 0-004M)

[HClO ₄]	[LiClO ₄]	H_0	$10^{5}k_{1}$	$10^{3}k_{3}$
	Serie	s 1 ($\mu = 1.0$) ^a)	-
0.10	0.90	1.86	2.44	128
0.20	0.80	1.55	12.0	157
0.30	0.70	1.36	30.5	160
0.50	0.20	1.11	98	163
0.60	0.40	1.02	155	155
0.80	0.20	0.87	268	147
1.00	0.00	0.75	410	129
	Series	$2~(\mu~{ m variab})$	ole ^b)	
0.07	0.93		1.15	2.35
0.10	0.00		0.066	0.066
ª k₃ ca	lculated with	h_0 . $b k_3$ ca	lculated with	[H+].

When the logarithm of the first-order rate constants of Series 1 were plotted against H_0 , the straight line shown in Figure 2 was obtained, which has the slope 2.04. Having regard to experimental errors, we consider this to signify that the overall conversion has a kinetic order of 2 in hydrogen ions. The mean value of the third-order rate constant k_3 is 150×10^{-3} sec.⁻¹ mole⁻² 1.². Since the conversion leads to rearrangement and disproportionation in comparable amounts, it must be concluded that each of these processes is of second order in hydrogen ions.

The two runs of Series 2 were done in order to isolate the salt effect and to provide a basis for approximate comparisons with conversion rates of other substituted hydrazobenzenes. One sees that on increasing the ionic strength from 0.1 to 1.0 with added lithium perchlorate, the rate, as measured by the third-order rate constant of the two-proton mechanism, is increased by a factor of 36.

Products.—They have been investigated by Jacobson,⁶ who identified some benzidine formed by loss of the chlorine substituent, together with major amounts of the diphenyline and o-semidine isomers of 4-chlorohydrazobenzene, and smaller amounts of the corresponding p-semidine and of the products of disproportionation. In one of his studies Jacobson did not employ his usual method of reducing an azo-compound by stannous chloride or zinc in acid solution, and allowing the presumably first-formed hydrazo-compound to rearrange in the solution in which it was produced. Instead, he reduced 4-chloroazobenzene with ammonium sulphide, and, after isolation of the hydrazo-compound, rearranged it with hydrochloric acid. His observation of the formation of a p-semidine in these conditions was an isolated one, and the quantity reported was minimal; but it had been accepted as significant, the idea (cf. Part XVIII⁷) that heavy-metal ions were necessary for p-semidine formation could not have been entertained. Jacobson's identifications, including that of the para-semidine, were later qualitatively confirmed by Večeřa and Petránek.⁸ And we confirm them in a kinetically specified reaction, and with the addition of quantitative estimates of most of the products. Our



FIGURE 2 Plot of the logarithm of the first-order rate constant of conversion of 4-chlorohydrazobenzene against H_0 for perchloric acid in '60%' aqueous dioxan at 0° and with $\mu = 1.0$. The line has slope 2.04

results are in Table 4. The chromatograms there referred to were developed with hexane on formamideethanol paper.

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Products from the acid conversion of 4-chlorohydrazobenzene

		2,4'-Diamino-	2-Amino-
	Bongidino	5-chloro-	5-chloro-
	Deliziume	orphenyi	phenylamme
$R_{\rm F}$	0.02	0.26	0.77
Colour 1 *	Red	Orange	Orange
Colour $2a * \dots$			Yellow
Colour 2b *	Blue	Purple	Purple
Mol. (%)	Traces	\gtrsim^{19} †	3 Ô
	4-Amino-		
	4'-chlorodi-	4-Chloro-	4-Chloro-
	phenylamine	azobenzene	aniline
$R_{\mathbf{F}}$	0.38	0.47	0.58
Colour 1 *	Red	Orange ‡	Yellow
Colour $2a * \dots$	Yellow	0,1	
Colour 2b	Violet-brown		Purple
Mol. (%)	20	15	16
* See note 1	inder Table 2.	† By differenc	e. † Original
colour		, , ,	+0

Our quantitative analyses were made on products formed in 0.1n- and in 1.0n-perchloric acid in the '60%'

⁸ M. Večeřa and J. Petránek, Coll. Czech. Chem. Comm., 1960, 25, 2005.

 ⁶ P. Jacobson and H. Strübe, Annalen, 1898, 303, 305; P. Jacobson, *ibid.*, 1909, 367, 320.
 ⁷ D. V. Banthorpe, A. Cooper, and C. K. Ingold, J. Chem.

⁷ D. V. Banthorpe, A. Cooper, and C. K. Ingold, *J. Chem.* Soc. (B), 1968, 609.

The results were identical. Thev dioxan solvent. were not quite as suggested by Jacobson, whose reductive conditions may have aided dechlorination. The benzidine formed by dechlorination was found by us only in very small amount, and the products which Jacobson describes as minor, including the p-semidine, arose in our work in quantitites of the same order of magnitude as those of Jacobson's main products. The summary is that, neglecting the small amount of dechlorination, the conversion resulted in 69% of rearrangement and 31% of disproportionation, and that the rearranged isomers consisted of 19% of the diphenyline, 30% of the o-semidine, and 20% of the p-semidine, reckoned on the total conversion. The lack of dependence of these figures on the acidity shows inter alia that rearrangement and disproportionation have the same kinetic order in hydrogen ions, so that they must be separately of second order in hydrogen ions. We know also that each is of first order in hydrazo-compound.

Similar conclusions follow for the formation of the separate rearrangement products. Too much of any of them is formed not to disturb the kinetics, if the kinetics of its formation were any different from those of the other isomers. Furthermore, too much of any one isomer is formed to allow the product composition to be independent of the acidity, if the kinetic order in hydrogen ions of its formation were any different from those of formation of the other isomers. Therefore the kinetic forms of all the simultaneous reactions, those leading severally to the diphenyline, the o-semidine, the p-semidine, and the disproportionation products, must be completely identical.

Non-appearance of Crossed Azo-products.—In all these studies we are taking opportunities to build up evidence on the mechanism of disproportionation. We have already concluded that the law of its kinetics is simply that it takes its kinetic form from the rearrangement which it is accompanying. In Part XVIII⁷ the point was added that crossed disproportionation processes can occur. This made it important to discover whether crossed azo-products can arise.

No unsymmetrical hydrazo-compound A·NH·NH·B has ever been observed to give, on disproportionation, besides the unsymmetrical azo-product A·N:N·B, either of the crossed azo-products of symmetrical type, A·N:N·A and B·N.N·B. Jacobson lists more than 50 examples which could exemplify this statement.⁹ Yet nobody, as far as we know, seems to have thought that any other result was possible, or that the non-observation of crossed azo-products might be significant for the mechanism of disproportionation. We know of no record showing that crossed azo-products were specifically looked for, and one cannot help wondering whether they were always looked for carefully enough to justify our accepting their non-formation as well-established.

We therefore examined the azo-product from the acid conversion of 4-chlorohydrazobenzene, looking especially for traces of 4,4'-dichloroazobenzene in the formed 4-chloroazobenzene. This is an easy thing to do by t.l.c. On chromatograms developed with cyclohexane on plates coated with alumina to a thickness of 0.25 mm., 4-chloroazobenzene has the $R_{\rm F}$ value 0.90 and 4,4'-dichloroazobenzene the value 0.10. We found no trace of the latter substance, although very small traces (much under 1%) would have been detectable.

Non-suppression of Disproportionation by Radical Inhibitors.-Both Večeřa and his co-workers 10 and Hammond and Clovis¹¹ have held the view that disproportionation might occur through a free-radical mechanism. Banthorpe, Bramley, and Thomas showed 12 that the production of radicals during benzidine rearrangements could not be detected by e.s.r. or the initiation of polymerisation. But this finding applies strictly to rearrangements, because the examples they selected for study were those in which rearrangement is unaccompanied by any significant amount of disproportion-We have therefore applied tests for dependence ation. on radicals to those of our conversions in which a substantial amount of disproportionation occurs.

A test suitable for application to the acid conversion of 4-chlorohydrazobenzene, which gives 31% of disproportionation, was to ascertain whether the amount of disproportionation relatively to rearrangement could be suppressed by operating in the presence of a large excess of a radical inhibitor. We converted 4-chlorohydrazobenzene (1 g.) with 1N-perchloric acid in the '60%' aqueous dioxan solvent in the presence of *m*-dinitrobenzene (10 g.). We then separated the azo-product, and estimated it spectrophotometrically. The proportion found was 16% of the total conversion. As shown in Table 4, the proportion found in the absence of the radical inhibitor was 15%. Clearly, the large excess of dinitrobenzene was making no difference.

Acid Conversion of 4,4'-Dichlorohydrazobenzene

Kinetics.—This acid conversion is slower by an order of magnitude than that of 4-chlorohydrazobenzene. The reaction of 4,4'-dichlorohydrazobenzene was studied kinetically in '60%' aqueous dioxan at 0°, with perchloric acid, in the concentration range 0.1-1.0N, as the source of hydrogen ions. Throughout, the formal ionic strength was made up to 1.0 by additions of lithium perchlorate.

All runs gave good first-order rate constants, thereby showing that the overall conversion is of first-order in hydrazo-compound. This is a significant result, because three-quarters of the total conversion consists in disproportionation, which stoicheiometrically involves two molecules of hydrazo-compound, though the kinetics of the process evidently depend on only one.

 ⁹ P. Jacobson, Annalen, 1922, 428, 90.
 ¹⁰ M. Večeřa, L. Synek, and V. Šteřba, Coll. Czech. Chem. Comm., 1960, 25, 1991.

¹¹ G. S. Hammond and J. C. Clovis, J. Org. Chem., 1963, 28, 3283.

¹² D. V. Banthorpe, R. Bramley, and J. A. Thomas, J. Chem. Soc., 1964, 2900.

As in the preceding examples, the acidity function needed to correlate rate with acidity is that appropriate to the acid, solvent, and ionic strength, as given in Part VIII.² The correlation of the first-order rate

TABLE 5

Dependence of the first-order rate-constant $(k_1 \text{ in sec.}^{-1})$ of the acid conversion of 4,4'-dichlorohydrazobenzene on the concentration and acidity function of perchloric acid in '60%' aqueous dioxan at 0°, and at the uniform ionic strength 1.0. (Initial concentration of hydrazo-compound about 0.004M throughout)

HClO ₄]	[LiClO ₄]	Ho	$10^{5}k_{1}$	$10^{3}k_{3}$
0.10	0.90	1.86	0.22	11.6
0.50	0.80	1.55	1.14	13.8
0.30	0.70	1.36	2.81	14.6
0.40	0.60	1.22	4.97	13.7
0.50	0.50	1.11	7.33	$12 \cdot 2$
0.60	0.40	1.02	11.3	11.4
0.70	0.30	0.94	15.9	12.0
0.80	0.20	0.87	$24 \cdot 1$	13.2
0.90	0.10	0.81	31.6	12.9
1.00	0.00	0.75	39.8	12.6

constants with the concentration of perchloric acid, and with the function $H_0 = -\log h_0$, from this acidity scale, is set out in Table 5. The logarithms of the first-



FIGURE 3 Plot of the logarithm of the first-order rate constant of conversion of 4,4'-dichlorohydrazobenzene against H_0 for perchloric acid in '60%' aqueous dioxan at 0° and with $\mu =$ 1.0. The line has slope 2.00

order rate constants, when plotted against the values of H_0 , give the line of Figure 3, whose slope is 2.00. Thus it is clear that the overall conversion, and, in particular, that disproportionation, has a kinetic order of 2 in hydrogen ions.

The mean third-order rate constant k_3 for the overall conversion is 12.8×10^{-3} sec.⁻¹ mole⁻² l.² for the '60%' solvent, with $\mu = 1$, and at 0°. This is larger by a factor 370 than the corresponding third-order constant for the two-proton reaction of 2,2'-dichlorohydrazobenzene in the same conditions. Evidently, the chlorosubstituents are more strongly deactivating in o- than

in p-positions. The rate-constant k_3 for 4,4'-dichlorohydrazobenzene is smaller than for hydrazobenzene by the factor 125 in the conditions stated.

Products.—They were investigated first by Calm and Heumann,¹³ who were able to find only the disproportionation products. Levin succeeced in finding the *o*-semidine rearrangement product.¹⁴ Večeřa and Petránek qualitatively identified all these products,⁸ whose formation we also confirm.

Our chromatograms, developed on formamide-ethanol paper with hexane with the results given in Table 6, showed only one rearrangement product isomeric with the original hydrazo-compound, namely the *o*-semidine. The other main products were those of disproportionation. There appeared also, but in quite small amount, a p-semidine formed with loss of one chlorine atom.

TABLE 6

Products from the acid conversion of 4,4'-dichlorohvdrazobenzene

	4-Amino-4'- chlorodi- phenyl-	2-Amino- 4',5-di- chlorodi- phenyl-	4,4'-Di- chloroazo-	4-Chloro-
	amine	amine	benzene	aniline
$R_{\rm F}$ (hexane)	0.32	0.74	0.96	0.57
Colour 1*	Red	Orange-	Orange †	Yellow
		brown	Ű,	
Colour $2a *$	Yellow	Yellow		
Colour $2b *$	Violet-	Purple		Purple
	brown	-		-
Mol. (%)	Traces	22	38	2 imes37
*	See note under	Table 2.	† Original colo	ur.

Quantitative determinations were made on the products formed in 0.1N- and in 1.0N-perchloric acid in the aqueous dioxan solvent. The proportions of the products formed at these acidities were identical. The conversion resulted in 22% of the one rearranged isomer, and 75% of the products of disproportionation. The lack of dependence of the product composition on the acidity shows again that the kinetic orders in acid of rearrangement and disproportionation are the same. It follows from the evidence of kinetics and product compositions taken together that rearrangement and disproportionation have identical kinetic forms, each being of first order in hydrazo-compound and second order in hydrogen ions.

Non-suppression of Disproportionation by Radical Inhibitors.—Such a high proportion of the acid conversion of 4,4'-dichlorohydrazobenzene results in disproportionation that the case seemed suitable for testing the dependence of the reaction on intermediate radicals by examining the effect of radical inhibitors on rate of conversion, as well as on product composition. Four radical inhibitors were tried, with the results in Table 7. Some of the rates suggest that some of the additives complex with the hydrazo-compound, but the rates as a whole show no evidence of the retardations that a radical

- ¹³ A. Calm and K. Heumann, Ber., 1880, 13, 1180.
- ¹⁴ P. Jacobson, Annalen, 1922, **427**, 149 (W. Levin, footnote).

mechanism would lead one to expect. Though differences of rate occurred, product compositions remained essentially the same.

TABLE 7

Effect of radical inhibitors on rate and products of acid conversion. [4,4'-Dichlorohydrazobenzene (0.11 g.) was converted with 1.0N-perchloric acid in '60%' aqueous dioxan at 0°. The first-order rate constant k_1 is in sec.⁻¹]

Additive	Amount (g.)	$10^{5}k_{1}$	Disproport.
None		39.8	75
<i>m</i> -Dinitrobenzene	0.2	72.6	75
Butyraldehyde oxime	0.3	69.3	75
Cyclohexene	0.5	$32 \cdot 3$	75
Catechol	0.2	43.4	75

Non-initiation of Polymerisation by the Conversion.-One of Banthorpe, Bramley, and Thomas's methods for testing for the production of radicals in hydrazorearrangements was by running these reactions in the presence of styrene, acrylonitrile, or methyl methacrylate, and comparing nephelometrically the polymerisation rate with that in a control experiment in which the hydrazo-compound was omitted.12 We used the same method, and the same polymerising monomers. After being washed with acid, alkali, and water, each monomer (5 g.) was added to a solution of 4,4'-dichlorohydrazobenzene (0·2 g.) in '60%' aqueous dioxan (50 ml.) containing 1.0N-perchloric acid. The control experiment was run concurrently. In no case was polymerisation in the presence of the reacting hydrazo-compound perceptibly faster than in its absence.

EXPERIMENTAL

Materials.-2,2'-Dichloroazobenzene was prepared from 2-chloronitrobenzene by reduction with zinc and sodium hydroxide as described by Vogel.15 Crystallised from ethanol, it had m.p. 135° (Found: C, 56.7; H, 3.2; Cl, 28.4; N, 11.4. Calc. for C₁₂H₈Cl₂N₂: C, 57.4; H, 3.2; Cl, 28.2; N, 11.2%). 4,4'-Dichloroazobenzene was prepared similarly, m.p. 187° (Found: N, 11.5%). 4-Chlorobenzene was prepared by condensation of nitrosobenzene with 4-chloroaniline as described by Jacobson and Loeb.¹⁶ The product was purified on an alumina column with benzene as eluent, crystallised from ethanol, and had m.p. 89° (Found: C, 65.8; H, 4.3; Cl, 16.3; N, 13.0. Calc. for $C_{12}H_9ClN_2$: C, 66.5; H, 4.2; Cl, 16.3; N, 13.0%). These chloro-azobenzenes were all reduced to the corresponding chloro-hydrazobenzenes with zinc and ammonium chloride, as described for the preparation of methoxy-hydrazo-benzenes in Part XVII.¹⁷ The hydrazo-compounds were always prepared immediately before use and were then colourless. 2,2'-Dichlorohydrazobenzene had m.p. 84°, 4-chlorohydrazobenzene m.p. 88°, and 4,4'-dichlorohydrazobenzene m.p. 120°.

A number of semidines were required to aid investigation in rearrangement products, and for the purpose of standardisation of spectrophotometric analyses. They were obtained by the reduction of nitrodiphenylamines, prepared by unambiguous synthetic methods. 1-Chloro-3,4-dinitrobenzene 18 m.p. 36°, was allowed to react with aniline in cold ethanol. The crystalline product, after being washed with acid and crystallised from ethanol, gave 5-chloro-2-nitrodiphenylamine, m.p. 112°. 2-Chloronitrobenzene and 4-chloroaniline were heated in equivalent amounts with sodium acetate in a sealed tube at $180-220^{\circ}$. The excess of reactants was removed by distillation in steam, and the residue was washed with acid, extracted with ethanol, and purified on an alumina column with benzene This gave 4-chloro-2'-nitrodiphenylamine, m.p. as eluent. 144°. 4-Chloro-4'-nitrodiphenylamine, m.p. 185°, was similarly prepared from 4-chloronitrobenzene and 4-chloroaniline. 1-Chloro-3,4-dinitrobenzene was condensed with 4-chloroaniline in ethanol to give 4,5'-dichloro-2'-nitrodiphenylamine, m.p. 154°. These nitro-compounds were all reduced to amino-diphenylamines in the same way, viz. in aqueous alcoholic solution with stannous chloride and hydrochloric acid. The semidines were extracted with ether from the basified solutions. 2-Amino-5-chlorodiphenylamine had m.p. 99°, 2-amino-4'-chlorodiphenylamine m.p. 118°, 4-amino-4'-chlorodiphenylamine m.p. 68°, and 2-amino-4',5-dichlorodiphenylamine m.p. 90°. All the m.p.'s quoted are consistent with those in the literature.

Bindschedler's Green was prepared and solvents were purified and degassed as described in Part XVII.¹⁷

Kinetic Methods.—The general methods described in Part XVII ¹⁷ were followed. The runs, being all more or less slow, were started in flasks: the Y-tube method was not employed. The methods of quenching and estimating residual hydrazo-compound were not all the same. In the runs with 2,2'-dichlorohydrazobenzene, quenching was accomplished with an excess of Bindschedler's Green, and the excess was determined by titration with titanous chloride. In the runs with 4-chloro- and 4,4'-dichlorohydrazobenzene, quenching was effected by addition to 1—2N-sodium acetate, and the unconsumed hydrazo-compound was titrated directly with Bindschedler's Green to a visual end-point.

Products.—The general procedure was as described in Part XVII. Table 8 contains some particulars of visible and u.v. absorption maxima, as determined by us for use in the spectrophotometric analysis.

TABLE 8

Wavelengths and extinction coefficients at absorption maxima

	Solvent	$\lambda (m\mu)$	ε
2,2'-Dichloroazobenzene	Ether	456	432
4-Chloroazobenzene	Ether	440	854
4,4'-Dichloroazobenzene	Ether	447	1072
3,3'-Dichlorobenzidine	Cyclohexane	282	23,300
2-Amino-5-chlorodiphenyl-	-		
amine	Cyclohexane	275	6690
4-Amino-4'-chlorodiphenyl-	2		
amine	Cyclohexane	288	7940
2-Amino-4', 5-dichlorodiphenyl-	•		
amine	Cyclohexane	308	7420

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¹⁷ D. V. Banthorpe and A. Cooper, *J. Chem. Soc.* (B), 1968, 605.

¹⁸ A. Laubenheimer, Ber., 1876, 9, 760.

¹⁵ A. I. Vogel, 'A Text-book of Practical Organic Chemistry,' Longmans, Green and Co., London, 1957, p. 631.

¹⁶ P. Jacobson and A. Loeb, Ber., 1903, 36, 4090.