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THE KINETICS OF BROMINATION OF ARYLIDENE ARYLHYDRAZONES

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The reaction of bromine with arylidene arylhydrazones to yield the hydrazidic bromides, ArCBr=N-NH-Ar', was first described forty years ago (1). Although the hydrazidic halides have since received considerable study (2), particularly as sources of 1,3-dipolar ions (2a) and azocarbonium ions (2b), no mechanistic or kinetic study has been made of the bromination reaction by which these can be prepared. This may be because of the rapidity of the reactions involved. We have now obtained kinetic data for this reaction.

The bromination reaction was followed by an amperometric method. The indicator system consisted of a platinum microelectrode, rotated at 750 rev. per minute by a Metrohm synchronous motor, and a silver-silver chloride reference electrode, separated from the water-jacketed reaction cell by a fine sintered glass disc and an agar plug saturated with potassium chloride. The electrodes were connected to a Metrohm Polarecord E261, which supplied the polarizing voltage (0.2 v.) and recorded the diffusion current as a function of time . The recorder deflection, less a small correction due to the residual current, was proportional to the concentration of the diffusible species, Br_2 and Br_3^- (3).

The reaction mixture used consisted of a 0.1M potassium bromide solution in a mixture of 70 volumes of acetic acid,

the acid having been previously fractionated from chromium trioxide, and 30 volumes of water, the water having been first deionized and then distilled from alkaline permanganate.
The substituted benzaldehyde p-nitrophenylhydrazones used as substrates were prepared (4a) in acetic acid and recrystallized to constant melting point from aqueous ethanol. A few days before a kinetic run, they were crystallized again (cf.5) from aqueous ethanol. Their sharp melting points indicate the presence of a single (syn-) isomer (6).

The reaction kinetics were studied with the solutions kept under nitrogen to minimize the formation of the hydroperoxide (5). However, since the reaction time was short (it varied from 20 to 300 seconds), the same results were obtained with air-saturated solutions. The reaction procedure was as follows. A small quantity (usually ca. 1.0 ml) of a solution (5 x 10^{-4}M, approximately) of bromine in 70:30 v/v acetic acid-water was introduced into 20 ml of the same solvent (containing KBr as already mentioned) in the reaction cell and, on attainment of a steady diffusion current (several seconds), approximately 1.0 ml of a solution of the hydrazone (ca. 1 x 10^{-2}M) in glacial acetic acid (4b) was added by means of a syringe through a self-sealing cap. Bromine concentration-time curves were then recorded and the rate constants were then derived from these.

In aqueous acetic acid containing excess bromide ion the active brominating species considered are molecular bromine and possibly tribromide ion (7) , the rate equation in the present instance being

$$-\frac{dBr_2}{dt} = k(Br_2)(\text{Hydrazone}) + k'(Br_3^-)(\text{Hydrazone})$$

$$= k_2(Br_2 + Br_3^-)(\text{Hydrazone}), \quad \text{where} \quad k_2 = \frac{k + k'K(Br^-)}{1 + K(Br^-)}$$

TABLE I

Rate Constants for the Bromination of Substituted Benzaldehyde p-Nitrophenylhydrazones, at 20.00 ± 0.05°C

Substituent	$10^2 k_1$ (sec.$^{-1}$)[a,b]	k_2(l.mole^{-1}sec.$^{-1}$)
p-nitro	2.16	50.5
p-cyano	2.56	62.6
p-bromo	4.72	115
p-chloro	4.75	116
p-fluoro	6.02	148
hydrogen	6.42	157
p-isopropyl	7.29	179
p-tolyl	8.61	211
p-methoxy	13.8	338
p-hydroxy	29.7	730
p-dimethylamino	23.1	565
m-nitro	2.68	65.5
m-bromo	3.96	97.0
m-chloro	3.98	97.5
m-tolyl	7.65	187

[a] Hydrazone concentration used 4.08 x 10^{-4}M; [b] All rate constants have been replicated 2 to 6 times; all are precise to better than ± 2%.

FIG. 1

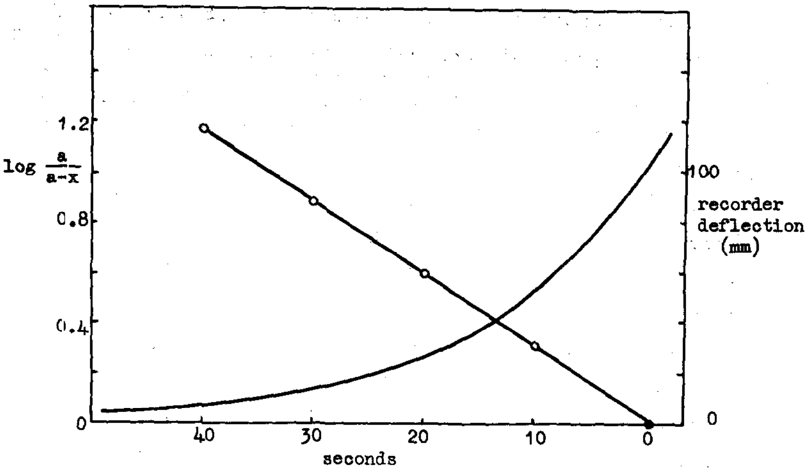


Fig. 1. Typical current-time curve for the bromination of benzaldehyde p- nitrophenylhydrazone.

FIG. 2

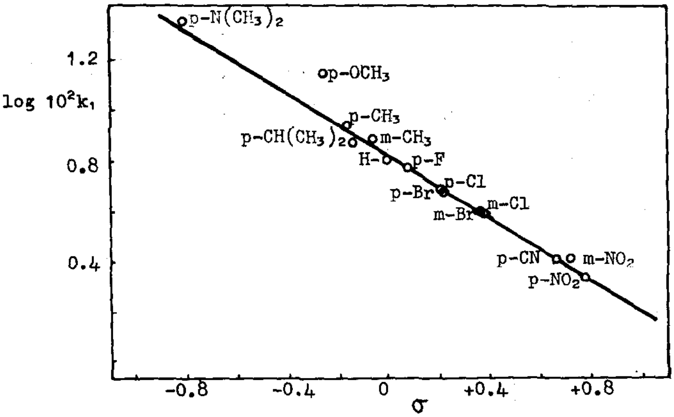


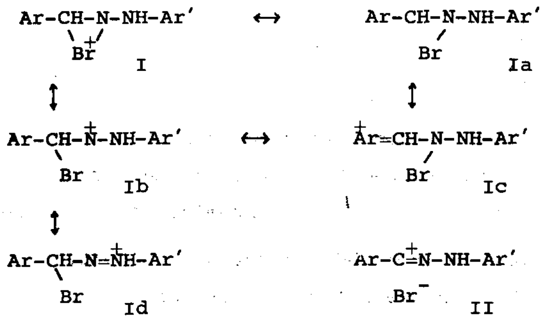
Fig.2. Hammett plot for the bromination of substituted benzaldehyde p-nitrophenylhydrazones at 20° in 70:30 acetic acid-water.

and K is the equilibrium constant for the reaction $Br_2 + Br^- \rightleftharpoons Br_3^-$. To avoid complications which were detected under other conditions, the kinetics were studied under pseudo-first order conditions with hydrazone:bromine ratios of 20:1. Under these conditions, the previous equation simplifies to

$$-\frac{dBr_2}{dt} = k_1(Br_2 + Br_3^-), \quad \text{where } k_1 = k_2(\text{hydrazone})$$

Good first order plots were obtained (Fig. 1) for various initial concentrations of the substrates, and these provide the rate data summarized in Table I. These rate values are 'global' rate constants i.e. do not separate the contributions due to molecular bromine and tribromide ion, a treatment recently extensively used by Dubois in his various bromination studies (8). For the nine para- and four meta-substituted benzaldehyde p-nitrophenylhydrazones studied (Table I), a plot (Fig. 2) of log k_1 against σ (9) gave an excellent correlation ($r = 0.997$, $s = 0.035$), with $\rho = -0.62$ (and log $k_0 = -1.175$). The rate data for the p-methoxy and p-hydroxy compounds fell far off the line, using σ or σ^+values.

The rate data are consistent with an azabromonium ion intermediate (I) which is resonance stabilized as follows:



The contributions of forms Ia and Ic impose positive charges on Ar and thus produce the negative ρ. The small value of ρ.

and its derivation from σ values, suggest that forms Ib and Id are major contributors. The ρ for the bromination of styrene, in acetic acid, is -2.23 (10). The contributing forms Ib and Id would certainly substantially reduce that. Related charge delocalization exists in the conjugate base of I, namely the azocarbonium ion (II), for whose formation we have recently (2b) obtained a ρ of -0.93. Structure (I) is even more effectively delocalized than (II), and one would therefore expect that the ρ for Ar in (I) should be less than -0.93. Our present value of -0.62 is thus eminently consistent with the data obtained earlier. A similar azabromonium ion is probably involved in the bromination of aliphatic enamines recently (11) reported. The large negative entropy values (calculated from rate data at 20, 10 and 0°, see Table II) indicate an ordered transition state and are close to the values given (10) for the bromination of styrene.

TABLE II

Thermodynamic Data

Substituent	$\Delta H^{\ddagger}$ k.cals	$\Delta S^{\ddagger}$ e.u.
p-nitro	9.6	-33.1
p-chloro	9.8	-30.8
p-fluoro	9.7	-30.7
hydrogen	9.7	-30.5
p-tolyl	9.7	-30.0
p-methoxy	11.2	-24.0

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