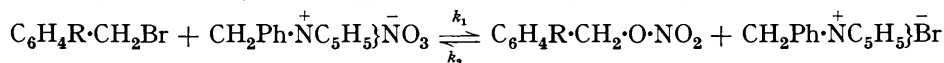


51. *The Mechanism of Aromatic Side-chain Reactions with Special Reference to the Polar Effects of Substituents. Part VII. Attack at a Saturated Carbon Atom by a Charged Ion.*

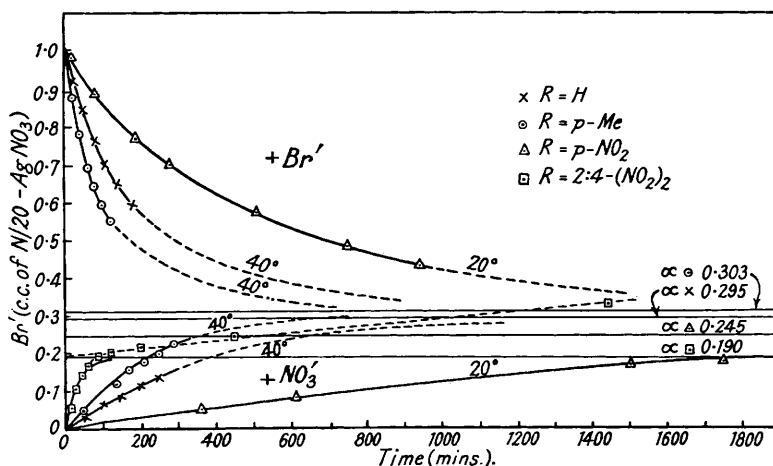
By JOHN W. BAKER and WILFRED S. NATHAN.

In Part III (J., 1935, 519) it was suggested that a study of the equilibrium



should furnish information regarding reactions involving attack at a saturated carbon atom by a charged ion instead of by a neutral molecule. In 0.025*M*-solution in dry acetone, this equilibrium is established at a velocity convenient for kinetic study, and this paper records the data obtained in such an investigation, more especially with reference to the effect of the substituent R upon the values of k_1 and k_2 .

FIG. 1.



It was first established, experimentally, that the same position of equilibrium was attained by starting from either pair of reactants (see Fig. 1, where typical results are plotted). Hence the kinetics of a reversible bimolecular reaction may be applied. If the initial concentrations (a) of the aryl bromide and of the arylpyridinium nitrate are equal, and x is the amount of aryl nitrate and arylpyridinium bromide formed at time t , we have

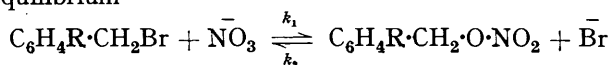
$dx/dt = k_1(a - x)^2 - k_2x^2$. If Δ is the value of x at equilibrium, integration of this equation in a manner similar to that employed by Bodenstein (*Z. physikal. Chem.*, 1894, **13**, 99) affords the relationship

$$k_1 = \frac{\Delta}{2at(a - \Delta)} \cdot \log_{e_d} \frac{\Delta a - x(2\Delta - a)}{a(\Delta - x)}$$

Use has been made of this expression to determine k_1 and k_2 independently from the experimental data, the procedure being to plot the values of the expression $f(x) = \log_{10}\{[\Delta a - x(2\Delta - a)]/a(\Delta - x)\}$ against time. The mean value of k_1 or k_2 was then derived from the slope of the best straight line drawn through the points so obtained. The results are summarised in Table I: concentration is expressed in g.-mols./l., time being in seconds. The experimental values of k_1 and k_2 are those obtained directly by using the appropriate pair of reactants. The calculated values are those derived from the relationship $K = k_1/k_2$ and the appropriate experimental value of k_2 or k_1 , respectively.

TABLE I.

Data for the equilibrium



in 0.025*M*-solution in dry acetone.

R.	Temp.	K.	$k_1 \times 10^4$.		$k_2 \times 10^4$.		Arrhenius <i>E</i> , kg.- cals.	k_1^R/k_1^H .	k_2^R/k_2^H .	10^{-11} PZ (at 40°) for	
			Exp.	Calc.	Exp.	Calc.				k_1 .	k_2 .
H	20°	0.177	<i>0.60</i>	0.60	<i>3.33</i>	3.4	18.4	1	1	—	—
H	40	0.175	<i>4.33</i>	4.4	<i>25.0</i>	25.0		1	1	0.03	0.17
<i>p</i> -Me	20	0.189	<i>1.1</i>	1.4	<i>7.3</i>	5.9	18.9	1.8	1.75	—	—
<i>p</i> -Me	40	0.189	<i>7.5</i>	8.8	<i>46.3</i>	40		2.0	1.9	0.11	0.72
<i>p</i> -Et	40	0.170	<i>7.1</i>	—	—	<i>41.7</i>	—	1.6 ₅	1.7	—	—
<i>p</i> -Bu ^v	40	0.189	<i>6.8</i>	—	—	<i>36.6</i>	—	1.6	1.5	—	—
<i>p</i> -NO ₂	20	0.105	<i>1.05</i>	1.04	<i>9.9</i>	9.9	18.9	1.7 ₅	3.0	—	—
<i>p</i> -NO ₂	40	0.105	<i>8.2</i>	9.3	<i>91</i>	78		1.9	3.1	0.13	1.21
2 : 4-(NO ₂) ₂ *	20	0.055	<i>4.0</i>	—	—	<i>76.7</i>	18.9	6.7	23	—	—
2 : 4-(NO ₂) ₂	40	0.055	<i>33.3</i>	—	—	<i>613</i>		7.7	24.5	0.52	9.5

The values printed in italics are those obtained from the more reliable experimental data and used in computing the other columns of the table.

* Although there is no doubt about the order of magnitude of the values for this compound, the actual figures are a little uncertain for the reason given on p. 241.

Confirmation that a true equilibrium is established is provided by some preliminary data, recorded in Table II, in which the initial concentrations of the aryl bromide (*a*) and the quaternary nitrate (*b*) were, respectively, 0.025 and 0.0125 g.-mols./l. Integration of the equation $dx/dt = k_1(a - x)(b - x) - k_2x^2$, giving the relationship when the initial concentrations of the two reactants are different, does not seem to be on record. We are greatly indebted to Dr. W. Wild, of this University, for the following integration. At equilibrium ($x = \Delta$), we have $k_2 = k_1(a - \Delta)(b - \Delta)/\Delta^2$; hence

$$dx/dt = k_1(a - x)(b - x) - k_1(a - \Delta)(b - \Delta)x^2/\Delta^2$$

and
$$\int_0^x k_1 ab \cdot dt = \int_0^x \left\{ 1 - \Delta \left(\frac{a+b}{ab} \right) \left(\frac{x}{\Delta} \right) - \left[1 - \Delta \left(\frac{a+b}{ab} \right) \right] \left(\frac{x}{\Delta} \right)^2 \right\}^{-1} dx$$

giving
$$k_1 = \frac{\Delta}{\{2ab - \Delta(a+b)\}t} \cdot \log_e \frac{ab\Delta - x\{\Delta(a+b) - ab\}}{ab(\Delta - x)}$$

From this expression the values of k_1 , given in Table II, were determined. From the experimental value of K , k_2 was then calculated. It will be observed that the values obtained approximate closely to those observed when equimolecular concentrations were employed (Table I).

TABLE II.

 $c_a = 0.025$, $c_b = 0.0125$ in dry acetone at 40°.

R.	K.	$k_1 \times 10^4$.	$k_2 \times 10^4$ (calc.).
H	0.18	4.5	25
<i>p</i> -Me	0.18	8.3	46
<i>p</i> -NO ₂	0.10	9.2	92

The values of k_1 and k_2 should be affected by at least three main factors, *viz.*, (1) the ease of anionisation of the bromine atom (k_1) or the nitrate group (k_2); (2) the ease of coordination of the nitrate ion (k_1) or the bromide ion (k_2); (3) orientation effects in the approach of the nitrate ion (k_1) or the bromide ion (k_2) to the carbon atom of the methylene group in the compound Ar·CH₂·X. Data obtained in earlier parts of this series suggested that some information with regard to factor (1) should be obtained by a comparison of the velocities of interaction (k_p) of the aryl bromide and of the aryl nitrate, severally, with pyridine in dry acetone solution. In such quaternary-salt formation all the important factors involved may be assumed to be nearly identical, with the exception of the relative ease of anionisation of the bromide and the nitrate group from the aryl compound. Thus, *ceteris paribus*, the relative velocities should be very closely related to (1). At 40° the experimental value of k_p for benzyl nitrate is 0.023×10^{-4} , *i.e.*, more than 200 times smaller than that (4.817×10^{-4}) for the corresponding reaction between pyridine and benzyl bromide under the same conditions.

Discussion.—Examination of the data summarised in Table I leads to the following conclusions.

1. Between 20° and 40° the position of equilibrium attained by any one pair of reactants is, within the experimental error, independent of temperature, *i.e.*, the activation energies of the forward and reverse reactions are identical.

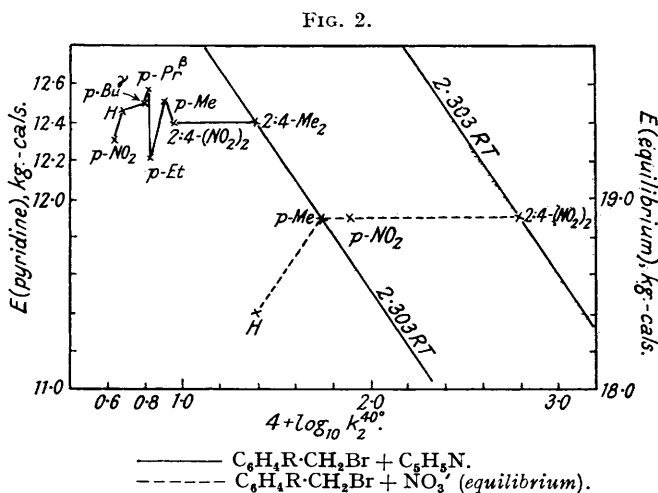
2. This energy of activation (18.5—19 kg.-cals.) is approximately constant, *i.e.*, it is independent of the nature of the substituent group in the aryl bromide or nitrate. It is considerably higher than that observed (*ca.* 12.5 kg.-cals.; cf. Parts III and IV) for the attack on the aryl bromide by the neutral molecules pyridine and α -picoline in the same solvent. This is in agreement with our earlier suggestion (Part III, p. 523) that, when the attack at a saturated carbon atom is by a negatively charged ion instead of by a neutral molecule, penetration of the electronic field surrounding the saturated atom by the attacking ion might involve an increase in the critical energy increment of the reaction.

3. In all cases the position of equilibrium is displaced largely in favour of the aryl bromide-quaternary nitrate pair, the value of k_2 being from 5 (H) to 20 (2:4-dinitro) times as great as that of k_1 . This larger value of k_2 might be due either (*a*) to the greater ease of ionisation of the C—O·NO₂ than of the C—Br linking, or (*b*) to the greater efficiency of the attack by the bromide ion than by the nitrate ion. Since, with pyridine, the aryl nitrate reacts very much more slowly than the aryl bromide (above), the former explanation would seem to be extremely improbable. Hence, it must be concluded that the attack by the bromide ion at the saturated carbon atom is much the more effective, so much so, indeed, that this factor quite outweighs the less ready anionisation of the nitrate group.

4. As expected, since both the forward and reverse reactions involve interaction between a neutral molecule and a charged ion, the value of PZ in the equation $k = PZe^{-E/RT}$ approximates to the normal value 2.8×10^{11} (Moelwyn-Hughes, "Kinetics of Reactions in Solution," p. 82), *i.e.*, P is of the order of unity. The increase in velocity ($k_1 + k_2$) caused by introduction of substituents into the aryl bromide (or nitrate) (an increase amounting to over 20-fold in the case of the 2:4-dinitro-compound) is, however, again found to be due, not to variation in E , but almost entirely to variation in the P factor. In view of the recent findings of Winkler and Hinshelwood (J., 1935, 1147) that the most important factor determining variation in the velocity of interaction of various alkyl halides with tertiary bases is the energy of activation, it seems desirable to emphasise that this does not appear to be so in the case of substituted benzyl halides. Both in their reaction with tertiary bases (Parts III and IV) and in the equilibrium reaction discussed

above, variations in velocity (admittedly of a relatively small magnitude) seem to be accounted for almost entirely by corresponding variations in the P factor. This is shown clearly in Fig. 2, where the plot of $\log k$ against E (for both reactions) is oriented to a line of standard slope $2.303RT$ (Winkler and Hinshelwood, *loc. cit.*; compare, however, Hughes, Ingold, and Shapiro, preceding paper).

The effect of substituent groups upon velocity. The lack of variation in E and the bimolecular kinetics of the above equilibrium suggest that, as in the case of attack by a neutral pyridine molecule, the reaction involves essentially the electron cycle $\overset{\ominus}{A} \xrightarrow{b} \text{CH}_2\text{Ar} \xrightarrow{a} \overset{\ominus}{X} \longrightarrow \text{A}-\text{CH}_2\text{Ar} + \overset{\ominus}{X}$, in which the factors (a , anionisation) and (b , electrostriction of the attacking negative ion) cannot be differentiated. Since the velocity is increased by introduction either of electron-repelling alkyl groups, which will facilitate (a), or of electron-attracting nitro-groups, facilitating (b), the hypothesis of critical initiation of the electron cycle previously proposed (Part IV) may also be applied in this case. In the equilibrium studied, however, the minimum velocity is observed with the unsubstituted compound. Alkyl substituents appear to increase the values of k_1 and k_2 to approximately the same



extent. This suggests that their polar influences are largely in the direction of increasing a pre-existing tendency to react by initiation of type (a) in both the aryl bromide and the aryl nitrate. Incidentally, it should be noted that their order of facilitation, $\text{Me} > \text{Et} > \text{Bu}^\gamma$, is again the reverse of that deduced from the operation of purely inductive ($+I$) effects, and confirms our earlier views (Parts V and VI) regarding the electron-release capacity of the methyl group in such systems.

The introduction of electron-attracting nitro-groups, however, although also causing an increase in the value of k_1 , effects a much greater increase in k_2 , *i.e.*, it favours preferentially, attack by the bromide ion.

It would appear probable that in the p -nitro- and the 2:4-dinitro-derivative the critical point has been shifted in favour of (preferential) initiation of type (b), and the dominant factor has now become the electrostriction of the attacking anion at the α -carbon. It is therefore in this region that the importance of the orientation of the attacking ion becomes paramount. The size and structure of the two ions are pertinent factors relevant to this question. The radius of the bromide ion, determined by X-ray examination of the crystals of metallic bromides (Landolt-Börnstein, Ergänzbd. II, p. 68), is 1.96 Å., and hence the most probable picture of the bromide ion in solution would represent it as a sphere of diameter approximately 3.92 Å. with one negative charge uniformly distributed on the surface. The nitrate ion has been shown (Goldschmidt, Freudenberg's "Stereochemie," 1933, p. 50) to possess a plane symmetrical structure, the distance between the nitrogen

and oxygen atoms being 1.23 Å. The ion is degenerate, two negative charges being distributed between the three oxygen atoms (located at the corners of an equilateral triangle) and one positive charge residing upon the nitrogen (situated at the centre of the triangle). Thus the bromide ion would seem to have a slightly larger collisional diameter. It is suggested that the difference in the effectiveness of attack by the two ions is mainly dependent upon their difference in structure. The spherical bromide ion, with its uniformly distributed negative charge, should be equally effective in promoting a critical collision no matter what is its orientation at the moment of approach to the saturated carbon atom. Orientation factors should, however, be much more important in relation to the similar attack by the nitrate ion. For any collision to be effective in promoting interaction, it seems probable that one of the oxygen atoms must be brought in close juxtaposition to the methylene carbon atom. Moreover a "flat-on" approach of the plane nitrate ion would present the central, positively charged nitrogen atom to the positive methylene carbon atom, thus bringing into play repulsive forces very unfavourable for the interpenetration of the electronic fields surrounding the reacting entities. Such orientation phenomena are at least in qualitative agreement with our results. The strong electron attraction of nitro-groups in the *o*- and *p*-positions to the side chain will greatly increase the positivity of the methylene carbon, thus facilitating the close approach of the symmetrically charged bromide ion, and so, greatly increasing the value of k_2 . This induced field at the methylene carbon atom should also favour the approach of the attacking nitrate ion, but, because of the rather special orientation necessary in this case, the increase produced in k_1 is of a much smaller magnitude.

EXPERIMENTAL.

Preparation of Materials.—Benzyl nitrate was prepared by Nef's method (*Annalen*, 1899, 309, 171). It was not readily purified, for it retained a small amount of an impurity (probably nitrogen-free), difficult to remove by distillation. Purification was controlled by heating the sample with an excess of pyridine at 100° for several hours, and determination of the nitrate ion so produced gravimetrically as nitron nitrate. Repeated distillation over silver nitrate gave the ester as a colourless liquid, b. p. 43°/0.5 mm. (Found: C, 55.5; H, 4.65; N, 9.5; NO₃', 39.9, 40.6. Calc. for C₇H₇O₃N: C, 54.9; H, 4.6; N, 9.2; NO₃', 40.5%).

p-Methylbenzyl nitrate was similarly prepared from *p*-methylbenzyl bromide and pure silver nitrate. A similar purification gave the nitrate as a colourless liquid, b. p. 60°/0.2 mm. (Found: NO₃', 36.6. C₈H₉O₃N requires NO₃', 37.1%). A sample, b. p. 73.0°/0.6 mm., from which the final sample was obtained by two further distillations, was analysed completely (Found: C, 58.0; H, 5.7; N, 7.7; NO₃', 34.6. C₈H₉O₃N requires C, 57.5; H, 5.4; N, 8.4; NO₃', 37.1%). The agreement between the values for N and NO₃' indicates that the impurity is probably nitrogen-free.

p-Nitrobenzyl nitrate (Staedel, *Annalen*, 1883, 217, 214) had m. p. 69°.

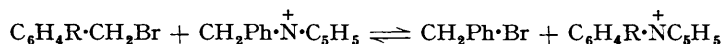
The substituted benzyl bromides were the specimens used for velocity determinations in earlier parts of this series. From them, the benzylpyridinium bromides were obtained by direct interaction with pyridine. Benzylpyridinium bromide is very hygroscopic and was dried over phosphoric oxide for several months before analysis (Found: Br, 31.86. Calc. for C₁₂H₁₂NBr: Br, 31.96%). *p*-Nitrobenzylpyridinium bromide has m. p. 218—220° (decomp.) (Found: Br, 27.08. Calc. for C₁₂H₁₁O₂N₂Br: Br, 27.09%). By interaction of the quaternary bromides with exactly the theoretical amount of aqueous silver nitrate were obtained *benzylpyridinium nitrate*, extremely hygroscopic (Found: NO₃', 26.1. C₁₂H₁₂O₃N₂ requires NO₃', 26.7%) and *p*-nitrobenzylpyridinium nitrate, m. p. 186° (decomp.) after crystallisation from 90% alcohol (Found: C, 52.2; H, 4.2. C₁₂H₁₁O₅N₃ requires C, 52.0; H, 4.0%).

The acetone was the unreactive sample used in Part IV.

Velocity Determinations.—The velocity measurements were effected by determination of the bromide ion by means of the micro-technique previously described (Part IV). Owing to their hygroscopic character, the solutions of the quaternary salts were made by tipping approximately the required amount of the dry salt from a small dried weighing tube directly into a known volume of dry acetone and determination of the weight used by difference. The solution was then diluted (in the thermostat) with the necessary volume of dry acetone to reduce the concentration to 0.05*M*. The aryl bromide or nitrate solutions (0.05*M*) were made up by direct weighing. 10 C.c. of each solution were then mixed at the temperature of the thermostat.

The position of equilibrium, in each case, was separately determined on solutions kept in sealed tubes in the thermostat for the necessary period.

In all cases, except that of the 2 : 4-dinitro-derivative, the plot of $f(x)$ (p. 237) against time gave, within experimental error, a straight time, from the slope of which the mean value of the velocity coefficient was determined. In the case of the 2 : 4-dinitrobenzyl bromide, the plot of the actual titrations against time showed the usual curve approaching an equilibrium value, followed by a slow further increase in titre directly proportional to time (see Fig. 1). The cause of this secondary reaction is unknown, but the equilibrium position was determined approximately by extrapolation of the straight line portion of the curve back to the titre-axis. For this reason the actual values of k_1 and k_2 are a little uncertain in this case, but their relative magnitude is beyond doubt. The possibility of reaction with the cation



has been considered, but owing to the small solubility of the nitrobenzylpyridinium bromide in dry acetone direct experimental investigation of this possibility was not possible.

Interaction of Benzyl Nitrate with Pyridine in Dry Acetone.—The velocity of quaternary salt formation was determined exactly as previously described in the case of the quaternary bromide, except that the reaction was followed by gravimetric determination of the nitrate ion produced. For this purpose the following micro-technique was evolved. A 2-c.c. sample of the reaction solution (originally 0.025*M* with respect to both reactants) was run into a specially constructed 15—20 c.c. separating funnel containing 2 c.c. of water and 10 c.c. of ether. After shaking, the aqueous layer was separated, and extraction of the ethereal layer repeated twice with 1 c.c. portions of water. The aqueous solution remaining in the short, drawn-out stem of the funnel was washed out with 0.5 c.c. of water. The combined aqueous extracts were evaporated on the steam-bath until their volume was reduced to 3—4 c.c. To the hot solution 3 drops of acetic acid and 25 drops of a standard nitron solution (Treadwell and Hall, "Analytical Chemistry," Vol. 2, p. 451) were added. The solution was allowed to cool to room temperature, and was then kept in ice for 30 minutes, access of air and light being minimised to prevent oxidation of the nitron. The precipitated nitron nitrate was collected in a weighed micro-crucible fitted with a fused-in porous bottom, washed with 2 c.c. of water saturated with nitron in small portions, and dried at 110° for 30 minutes before weighing. Under these conditions the factor $\text{NO}_3'/\text{nitron nitrate} = 16.79\%$. The accuracy of the method was tested first on pure sodium nitrate in 0.025*N*-solution (Found : NO_3' , 71.3, 71.5. Calc. for NaNO_3 : NO_3' , 72.9%), and then with 2 c.c. of a 0.025*M*-solution of benzylpyridinium nitrate in dry acetone, treated as above (Found : NO_3' , 26.57, 26.42. Calc. for $\text{C}_{12}\text{H}_{12}\text{O}_3\text{N}_2$: NO_3' , 26.1%). A control experiment, in which a solution of benzyl nitrate in acetone was similarly treated, gave no precipitate of nitron nitrate.

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