792. *Intermediates in Aralkyl Systems. Part II.* Kinetics and Mechanism of Substitution of Diphenylmethyl Bromide by Anionic Reagents in Nitromethane.*

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The reactions of tetraethylammonium bromide, chloride, and azide with diphenylmethyl bromide were investigated in nitromethane. The rates are analysed in terms of concurrent first- and second-order processes. The kinetics of the first-order component embody three features: (*a*) the initial rates of the various substitutions are practically the same, (*b*) the ionic-strength effects are similar and positive, and (*c*) in the non-symmetric substitution by chloride ions, common ions seem to be able to depress the entire first-order component. The kinetics of the second-order components are subject to a negative salt effect. It is suggested that the first- and second-order components represent a uni- and a bi-molecular substitution process respectively.

For the more detailed investigation of non-solvolytic unimolecular substitutions, S_N1, it is advantageous to cut out simultaneous solvolyses. A solvent must be used which sufficiently ionises the substrate to promote the desired type of substitution, but is insufficiently nucleophilic to be decomposed by the carbonium ion formed. Nitromethane partially satisfies these demands. Although it is not entirely inert towards a relatively high concentration of carbonium ions, whether added in bulk [1] or present in thermodynamic equilibrium with the substrate,[2] it is sufficiently unreactive towards alkyl halides for which the ionisation process is rate-determining.[3a,b,4] Diphenylmethyl bromide suggested itself as an aralkyl halide free from elimination reactions and at the same time likely to exhibit in nitromethane, at least in part, a unimolecular mechanism of substitution.

Our first purpose was to test how far it is necessary, without invoking stereochemistry,[5] to elaborate the S_N1 ionisation scheme in nitromethane to include a partly heterolysed but undissociated intermediate. Our second was to examine under non-solvolytic conditions in a sufficiently polar medium whether, by increasing the concentration or the nucleophilic power of the anionic substituting agent, a behaviour intermediate between

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* The paper " The Ionisation of TriphenylmethylChloride in Nitromethane," *J.*, 1958, 240, is regarded as Part I in this Series.

[1] Burton and Cheesman, *J.*, 1953, 832.

[2] Pocker, *J.*, 1958, 240.

[3] (*a*) Gelles, Hughes, and Ingold, *J.*, 1954, 2924; (*b*) de la Mare, Hughes, Ingold, and Pocker, *ibid.*, p. 2930.

[4] Pocker, *J.*, 1959, 1179.

[5] Pocker, " Kinetics and Mechanisms of Exchange and Racemisation in Aralphyl Halides," paper presented at the Informal Faraday Soc. meeting on Isotopic Exchange Reactions in Leeds, 26th Sept., 1958. Abstracts appear in *Trans. Faraday Soc.*, 1959, **55**, 1266.

S_N1 and S_N2 would be induced (*i.e.*, borderline mechanism), or whether two concurrent and independent processes would occur.[6a–l]

(1) *Reaction of Diphenylmethyl Bromide with Bromide ions.*—Bromide ions were supplied as tetraethylammonium bromide labelled with radiobromine, ^{82}Br, of half-life 36 hr. The rate of isotopic exchange was studied over a range of reagent concentrations. The first-order rate coefficients of exchange, k_E, are given in Table 1. They were calculated by a method (Experimental) which allows for radioactive decay and dilution and for any reaction which occurs during mixing. The results indicate that the rate of exchange, v_E, is best expressed by the equation:

TABLE 1. *First-order rate coefficients,* k_E *(sec.*$^{-1}$*), of exchange between diphenylmethyl bromide and isotopically labelled bromide ions in nitromethane at* 25·0°.

(a)								
$10^2[Ph_2CHBr]$ ...	2·0	2·0	2·0	2·0	2·0	0·2	1·0	4·0
$10^2[NEt_4{}^{82}Br]$ ...	0·1	0·2	0·5	1·0	2·0	0·2	1·0	1·0
10^5k_E	1·93	2·08	2·65	3·60	5·35	2·06	3·65	3·5

(b)						
$10^2[Ph_2CHBr]$...	2·0	2·0	2·0	2·0	2·0	2·0
$10^2[NEt_4{}^{82}Br]$ ...	0·2	0·2	0·2	0·2	0·2	0·2
$10^2[NEt_4ClO_4]$...	0·3	0·8	1·8	2·8	5·8	3·8
10^5k_{obs}	2·16	2·20	2·30	2·36	2·64	2·47
μ	0·005	0·010	0·020	0·030	0·060	0·040
$10^5k_1{}^{\mu}$	1·80 *	1·84 *	1·94 *	2·00 *	2·28 *	2·11 *

$10^2[Ph_2CHBr]$	2·0	2·0	2·0
$10^2[NEt_4{}^{82}Br]$	0·1	0·1	0·1
$10^2[NEt_4ClO_4]$	1·9	2·9	5·9
10^5k_E	2·13	2·18	2·44
μ	0·020	0·030	0·060
$10^5k_1{}^{\mu}$	1·95 †	2·00 †	2·26 †

* Calculated from k_{obs} by using $k_2[NEt_4Br] = 0{\cdot}36 \times 10^{-5}$ sec.$^{-1}$.
† Calculated from k_{obs} by using $k_2[NEt_4Br] = 0{\cdot}18 \times 10^{-5}$ sec.$^{-1}$.

(c)				
$10^2[Ph_2CHBr]$	2·0	2·0	2·0	2·0
$10^2[NEt_4{}^{82}Br]$	2·0	2·0	2·0	2·0
$10^2[NEt_4ClO_4]$	—	1·0	2·0	4·0
10^5k_E	5·35	5·30	5·26	5·16

$$v_E = k_E[Ph_2CHBr] = k_1[Ph_2CHBr] + k_2[Ph_2CHBr][NEt_4Br]$$

where at low ionic strength $10^5k_1 = 1{\cdot}75 \pm 0{\cdot}05$ sec.$^{-1}$ and $10^5k_2 = 180 \pm 5$ sec.$^{-1}$ l. mole^{-1}. To obtain the dependence of k_1 on the ionic strength, the effect of added tetraethylammonium perchlorate was investigated in detail (Table 1*b*). When $[NEt_4Br] = 0{\cdot}002$M, the contribution of the second-order component, $k_2[Ph_2CHBr][NEt_4Br]$ is only 15% of the overall rate of exchange, so that variations in k_{obs} can be analysed as being mainly due to variations in k_1. This analysis is confirmed by the more limited range of results obtained with $[NEt_4Br] = 0{\cdot}001$M, where the second-order component is only 7·5% of the overall rate of exchange. At higher concentrations of saline bromide the dependence of k_{obs} on the ionic strength (Table 1*c*) is such as to suggest that k_2 itself is subject to a negative salt effect as would accord with its being a rate coefficient of a bimolecular S_N2 reaction between a neutral molecule and an anion.

The stabilisation effect by means of an ionic atmosphere of the transition state of the unimolecular component can to a first approximation be expressed [7] by

$$\log (k_1{}^{\mu}/k_1{}^0) = (0{\cdot}912 \times 10^{16})\sigma\mu/(DT)^2$$

where $k_1{}^{\mu}$ is the first-order rate coefficient of ionisation in a solution of ionic strength μ and $k_2{}^0$ is the limiting value as the ionic strength approaches zero. The logarithmic ratio depends on the ionising molecule through a parameter σ of the transition state, the dielectric constant ($D = 36$ at 25·0°), and absolute temperature ($T = 298°$). This is a

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[6] (*a*) Gleave, Hughes, and Ingold, *J.*, 1935, 236; (*b*) Baker and Nathan, *J.*, 1935, 1842; (*c*) Hughes, Ingold, and Shapiro, *ibid.*, 1936, 228; (*d*) Baker, *Trans. Faraday Soc.*, 1941, **37**, 632; (*e*) Winstein, Grunwald, and Jones, *J. Amer. Chem. Soc.*, 1951, **73**, 2700; (*f*) Swain and Langsdorf, jun., *ibid.*, p. 2813; (*g*) Dewar, *Ann. Reports*, 1951, **48**, 118; (*h*) Bird, Hughes, and Ingold, *J.*, 1954, 634; (*k*) Gold, *ibid.*, 1956, 4633; (*l*) Kohnstam, Queen, and Shillaker, *Proc. Chem. Soc.*, 1959, 158.

[7] Bateman, Church, Hughes, Ingold, and Taher, *J.*, 1940, 979.

limiting law for dilute solutions where the dissociation of the saline species is practically complete. It follows from the above equation that a plot of log k_1^{μ} against μ (= $[NEt_4ClO_4]$ + $[NEt_4Br]$) should be linear with intercept log k_1^0 and slope $0{\cdot}788 \times 10^8$. From the slope, using the data for k_1^{μ} given in Table 1*b*, one obtains $\sigma = 2{\cdot}45 \times 10^{-8}$. If we treat the change separation in the transition state as a pair of point charges, $\pm ze$, separated by distance d, then, $\sigma = z^2d = 2{\cdot}45$ Å. The normal carbon–bromine bond distance being $r_1 = 2{\cdot}05$ Å, one can evaluate $(d - r_1)$ for different values of z:

z	0·8	0·9	0·95	1
d (Å)	3·84	3·03	2·73	2·45
$d - r_1$ (Å)	1·79	0·98	0·68	0·3

The distance $d - r_1$ is not, however, the bond elongation in the transition state because the positive charge is not localised on the methyl-carbon atom. The purpose of the above calculation is, however, to emphasise that even if the positive charge was localised on the methyl carbon one could still only obtain a rough value for the polarity of the activated complex. To proceed any further with such calculations either the charge or the amount of separation would have to be assumed, so that any consideration of the amount of covalent binding in the transition state is necessarily inconclusive.

(2) *Reaction of Diphenylmethyl Bromide with Chloride Ions.*—Chloride ions were supplied as tetraethylammonium chloride of normal isotopic abundance as well as labelled with ^{36}Cl. The radioactive salt was employed in order to overcome the uncertainty introduced by the hydrolysis of the alkyl halide when the saline material is extracted into water. The radioactive assay method proved to be particularly valuable in determining the extent of reaction in runs in the presence of high concentrations of saline bromide. The first-order coefficients of disappearance of diphenylmethyl bromide fall progressively within any given run. A set of initial first-order rate coefficients, k_i, is shown in Table 2 which illustrates that the initial first-order rate coefficients, $k_{i,\text{obs}}$, can be expressed with an accuracy of ±3% by the equation

$$k_i\,(\text{sec.}^{-1}) = k_1^{\mu} + (12 \times 10^{-5})[NEt_4Cl]$$

where k_1^{μ} is the first-order rate coefficient of the unimolecular component of displacement in a medium of ionic strength μ. Values for k_1^{μ} were independently obtained in a set of runs recorded in Table 2*b*. These are in good agreement with the corresponding values obtained in symmetrical exchange (Table 1*b*).

TABLE 2. *Initial first-order rate coefficients,* k_i *(sec.*$^{-1}$*), of displacement of bromine from diphenylmethyl bromide by chloride ions in nitromethane at* 25·0°.

(*a*) $10^2[Ph_2CHBr]$	2·6	2·6	2·6	2·6	2·6	2·6
$10^2[NEt_4Cl]$	0·07	0·141	0·282	0·527	1·0	2·0 *
10^5k_i	$1{\cdot}75^R$	$1{\cdot}75^R$	$1{\cdot}78^P$	$1{\cdot}86^R$	$1{\cdot}95^P$	$2{\cdot}15^R$

R, Radioactive method, using $NEt_4{}^{36}Cl$; P, Potentiometric titrations.
* Run with 0·020M-$Bu^n{}_4NCl$ gave $10^5k_i = 2{\cdot}12$.

(*b*) $10^2[Ph_2CHBr]$	2·6	2·6	2·6	2·6	2·6
$10^2[NEt_4Cl]$	0·282	0·282	0·282	0·282	0·282
$10^2[NEt_4ClO_4]$	0·282	0·718	1·718	2·82 †‡	10·0
10^5k_i	1·79	1·83	1·90	1·95	2·56
μ	0·00564	0·010	0·020	0·031	0·103
$10^5k_1^{\mu}$	1·76	1·80	1·87	1·92	2·53

† Run with 0·0282M-$Bu^n{}_4NClO_4$ gave $10^5k_i = 1{\cdot}93$. ‡ Run with 0·0282M-NEt_4BF_4 gave $10^5k = 1{\cdot}98$.

(*c*) $10^2[Ph_2CHBr]$	2·6	2·6	2·6	2·6
$10^2[NEt_4Cl]$	0·282	0·282	0·282	0·282
$10^2[NEt_4Br]$	0·282	0·527	2·82	10·0
10^5k_x	1·36	1·10	0·470	0·09
μ	0·00564	0·00809	0·03102	0·103
$10^5k_{1,\text{calc}}$	1·33 §	1·06 §	0·445 §	0·07 §

§ Where $10^5k_{1,\text{calc}} = 10^5k_1^{\mu}/(0{\cdot}35[Br^-]/[Cl^-] + 1)$ and $10^5k_2(NEt_4Cl) = 0{\cdot}0336$ sec.$^{-1}$.

The progressive fall of the forward rate within any given run is satisfactorily accounted for by the ionisation scheme

$$Ph_2CHBr \underset{k_{Br^-}}{\overset{k_1}{\rightleftharpoons}} Ph_2CH^+ + Br^- \xrightarrow{+ Cl^-,\ k_{Cl^-}} Ph_2CHCl + Br^-$$

consideration being taken of the concurrent bimolecular reaction,

$$Ph_2CHBr + Cl^- \xrightarrow{k_2} Ph_2CHCl + Br^-$$

The presence of bromide ions reduces the unimolecular component of displacement by chloride ions so that

$$k_{obs} = \frac{k_1^{\mu}}{(k_{Br^-}[Br^-]/k_{Cl^-}[Cl^-]) + 1} + k_2[NEt_4Cl]$$

The progressive fall in k_{obs} in any given run is well represented by the above equation of $k_{Br^-}/k_{Cl^-} = 0{\cdot}35$. Added tetraethylammomium bromide depresses the initial rate of reaction (Table 2*a*) and here too a value of 0·35 for k_{Br^-}/k_{Cl^-} accounts satisfactorily for the observed depressions. This is illustrated at a low chloride ion concentration where $[NEt_4Cl] = 0{\cdot}0028$M, where the contribution of the bimolecular component is relatively small; $k_2\ [NEt_4Cl] = 0{\cdot}0336 \times 10^{-5}$ sec.$^{-1}$. It will be noticed that in the presence of sufficient saline bromide one can suppress the unimolecular component almost entirely, and that k_{Br^-}/k_{Cl^-} is throughout *ca.* 0·35. This indicates that the competitions between bromide and chloride ions take place at one and the same stage of ionisation.

(3) *Reaction of Diphenylmethyl Bromide with Azide Ions.*—The ions were introduced as tetraethylammonium azide and the progress of the reactions determined titrimetrically by following disappearance of azide ion, $-dN_3^-/dt$. The initial first-order rate coefficients of disappearance of diphenylmethyl bromide, $-d[Ph_2CHBr]/[Ph_2CHBr]dt = k_i$, calculated from such data, are given in Table 3. The initial first-order rate coefficients are satisfactorily expressed by the linear expression, $k_i = k_1 + k_2[NEt_4N_3]$, where at low ionic strength $10^5k_1 = 1{\cdot}75$ sec.$^{-1}$ and $10^5k_2 = 23{,}000$ sec.$^{-1}$ l. mole^{-1}. The magnitude of the bimolecular component of displacement by azide ions is so large that it proved impracticable to measure the intensity of the common-ion mass-law effect, k_{Br}/k_{N_3}. Rough measurements indicate that k_{Br^-}-$k_{N_3^-}$ is approximately $\frac{1}{5}$.

TABLE 3. *Initial first-order rate coefficients, k_i (sec.$^{-1}$), of displacement of bromine from diphenylmethyl bromide by azide ions in nitromethane at 25·0°.*

$10^2[Ph_2CHBr]$	0·191	0·191	1·91	1·91	1·91	1·91
$10^2[NEt_4N_3]$	0·0045	0·009	0·150	0·24	0·49	0·67
10^5k_i	2·78	3·8	36	57	112	159

Discussion.—(*a*) In nitromethane, the first-order component of substitution of diphenylmethyl bromide by chloride, radiobromide, and azide ions is practically the same: $k_1 = 1{\cdot}75 \times 10^{-5}$ sec.$^{-1}$. On the other hand, the second-order component for substitution by azide ions is 128 times larger than that for bromide ions and 1900 times larger than that for chloride ions, while the relative capacity for capturing Ph_2CH^+ is: N_3^- [*ca.* 5) > Cl^- (2·86) > Br^- (1·0). (*b*) Added perchlorate ions increase the first-order component of substitution but decrease the second-order component. (*c*) Common ions decrease the first-order component of non-symmetric substitution, and can suppress practically the entire first-order component. The intervention coefficient is the same up to *ca.* 90% repression of rate.

Results (*a*), (*b*), and (*c*) suggest that the first- and second-order components represent a uni- and a bi-molecular substitution respectively. The unimolecular substitution seems to proceed through free carbonium ions.

EXPERIMENTAL

Materials.—Nitromethane was dried, fractionated, and chromatographed as previously described.[2] Diphenylmethyl bromide was prepared (*a*) by the bromination of diphenylmethane and (*b*) from diphenylmethanol and phosphorus tribromide. The products from (*a*) and (*b*) were practically identical after distillation, having b. p. 140—145°/3 mm. Tetraethylammonium salts were prepared as before.[8]

Kinetic Measurements.—Temperature control was ±0·01° at 25·0°. Reaction mixtures (50 c.c.) were prepared by the addition of the necessary amount of previously prepared standard solutions of reagents and solvent, both preheated to 25·0°, to a weighed sample of diphenylmethyl bromide. In reactions with tetraethylammonium azide, aliquot portions were delivered into dry acetone at −80° and titrated with standard acid, lacmoid being used as indicator (in acetone azide ions behave as a strong base towards lacmoid).

Radioactive Runs.—(*a*) Known volumes of the reaction mixture containing diphenylmethyl bromide and tetraethylammonium radiobromide, with or without saline perchlorate, were withdrawn and run into 100 c.c. of cold dry ether. The precipitated salt was washed with fresh ether and dissolved in 15 c.c. of water, and its radioactivity measured with a liquid Geiger counter and standard scaling equipment. Each sample was counted twice. From the decay curves, which corresponded within experimental error with those expected for ^{82}Br, values were read to give counts for each sample at the same but otherwise arbitrary time. The bromide content of each sample was also determined and thus the activities as measured were corrected to give specific activities, referring in each experiment to the same arbitrary concentration of bromide ion. First-order rate coefficients, k_{obs} (sec.$^{-1}$), were deduced from the formula: [9]

$$k_{\text{obs}} = \frac{2{\cdot}303b}{(a + b)t} \log \left\{1 - \frac{x_0}{c}\left(1 + \frac{b}{a}\right)\right\} \Big/ \left\{1 - \frac{x}{c}\left(1 + \frac{b}{a}\right)\right\}$$

where t is the time in sec., a and b the concentrations of diphenylmethyl bromide and tetraethylammonium bromide respectively, $c - x_0$ and $c - x$ the specific activities at kinetic zero and time t respectively, and c is the specific activity of the initial reaction mixture. A convenient way to use this formula is to plot $\log \{1 - (a + b)x/aC\}$ against t and multiply the slope of the line by $-2{\cdot}303b/(a + b)$.

(*b*) Radiochloride, ^{36}Cl, is a long-lived isotope and requires no correction for decay. The reaction with diphenylmethyl bromide is a non-symmetric exchange and a loss in the radioactivity of the saline precipitate is a direct consequence of a decrease in the chloride-ion concentration. Aliquot portions were run into 100 c.c. of dry cold ether, and the precipitate was washed with ether, dissolved in water, and counted as in (*a*). If C_0 and C_t are the initial count and the count at time t respectively, then $[\text{Cl}^-]_t = [\text{Cl}^-]_0 C_t/C_0$ and

$$k_{\text{obs}} = \frac{2{\cdot}303}{t} \log \frac{[[\text{Ph}_2\text{CHBr}]_0}{[\text{Ph}_2\text{CHBr}]_0 - \{[\text{Cl}]_0 - [\text{Cl}]_t\}}$$

Isolation of Products.—Diphenylmethyl azide was isolated in 96% yield from the reaction with tetraethylammonium azide. Diphenylmethyl chloride was isolated in 95% yield from the reaction with *excess* of tetraethylammonium chloride.

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[8] Pocker, *J.*, 1959, 2319.

[9] Hughes, Ingold, Mok, Patai, and Pocker, *J.*, 1957, 1220.