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NUCLEOPHILIC SUBSTITUTION REACTION OF BENZYL BROMIDE WITH *N,N*-DIMETHYLANILINE: SIGNIFICANCE OF EQUILIBRIUM CROSS-INTERACTION CONSTANT

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Kinetic studies on the reversible reactions of benzyl bromides with *N,N*-dimethylanilines were carried out for both the forward (k_f) and reverse (k_r) directions. The equilibrium constants, *K* were calculated using the ratio k_f/k_r and the equilibrium cross-interaction constant, ρ^e_{XY} was determined. The ρ^e_{XY} value was shown to represent a maximum intensity of interactions between substituents X and Y through covalent bonds within a molecule. The normalized values of ρ_X (ρ_{nuc}) and ρ_{XY} indicate that in the transition state the fractional development or loss of polar and resonance interactions in the benzyl system are imbalanced or non-perfectly synchronized. In the forward reaction the fractional loss of resonance interaction becomes enhanced, whereas in the reverse reaction the fractional development of resonance interaction lags behind the corresponding changes of polar interaction by *ca* 45%.

INTRODUCTION

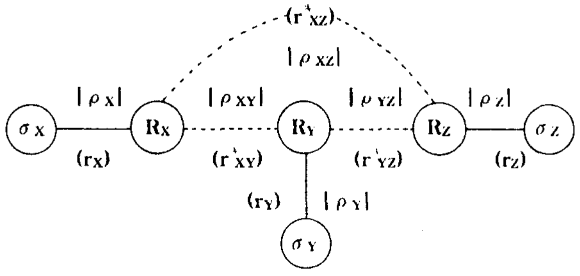
When two reactants *i* and *j* interact, the effect of substituents in the two, σ_i and σ_j, on the reactivity can be expressed as a Taylor series expansion of $\log k_{ij}$ around $\sigma_i = \sigma_j = 0$ (for which $k_{ij} = k_{00}$). Neglect of pure second-order and higher order terms, $\rho_{ii} = \rho_{jj} = \rho_{iij} = \rho_{ijj} = 0$, leads us to a very simple second-order form:[1]

$$\log(k_{ij}/k_{00}) = \rho_i\sigma_i + \rho_j\sigma_j + \rho_{ij}\sigma_i\sigma_j \qquad (1)$$

It has been shown that the cross-interaction constant, ρ_{ij}, causes the non-additivity of the two substituent effects[2] and has a highly important mechanistic significance as an activation parameter related to changes in the force constant[3] (or changes in the intensity of interaction) of the two interacting atoms in species *i* and *j* from the reactant to transition state (TS). Thus the notation used in equation (1), ρ_{ij}, is a simplified version of the proper one, $\Delta\rho^{\ddagger}_{ij}$:

$$\rho_{ij} \equiv \Delta\rho^{\ddagger}_{ij} = \rho^{\ddagger}_{ij} - \rho^{0}_{ij} \qquad (2)$$

For example, in an S_N2 TS (Scheme 1), *i* and *j* in equations (1) and (2) represent the nucleophile (X), substrate (Y) or leaving group (Z). When a bond is being formed in an S_N2 process, ρ^0_{XY} is zero since initially the two, X and Y, can be considered to be at a distance of infinity and non-interacting;[3] ρ_{XY} ($\equiv \Delta\rho^{\ddagger}_{XY}$) is therefore equal to the intensity of interaction at the TS, $\rho^{\ddagger}_{XY}$, which will be large at a close distance, i.e. for a greater degree of bond formation.[3] This means that the magnitude of ρ_{XY} ($\equiv \Delta\rho^{\ddagger}_{XY} = \rho^{\ddagger}_{XY}$) provides a measure of the extent of bond making in the TS; in the limiting case of S_N1, no bond making takes place in the TS so that ρ_{XY} ($= \rho^{\ddagger}_{XY} = 0$) vanishes.[1,3,4] Likewise, the magnitudes of ρ_{YZ} and ρ_{XZ} reflect the extent of bond breaking and the overall tightness of the TS, respectively.[3]



Scheme 1

It is of interest, however, to see what the significances of the cross-interaction constants for an equilibrium process, ρ^e_{XY}, ρ^e_{YZ} and ρ^e_{XZ}, are. In this work, we attempted to determine and apply such an equilibrium cross-interaction constant in a reversible S_N2 process using the reactions of benzyl bromides (BB) with *N,N*-

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dimethylanilines (DMA), in acetone at 45·0 °C:

$$XC_6H_4N(CH_3)_2 + YC_6H_4CH_2Br \underset{k_r}{\overset{k_f}{\rightleftharpoons}} YC_6H_4CH_2\overset{+}{N}(CH_3)_2C_6H_4X + Br^- \quad (3)$$

$X = p-CH_3$, $m-CH_3$, H, $p-Br$ or $m-Cl$

$Y = p-CH_3$, $m-CH_3$, H, $p-Cl$ or $m-Cl$

RESULTS AND DISCUSSION

In the forward reaction, a pseudo-first-order condition was kept throughout by reacting more than *ca* 500-fold of DMA relative to the substrate (BB) concentration. In order to test the effect of the DMA concentration on the observed pseudo-first-order rate constant, k_{obs}, we varied the [DMA] more than tenfold from 0·025 to 0·349 M as shown in Figure 1. We note that the intercept, k_1 in the equation

$$k_{obs} = k_1 + k_2[\text{DMA}] \quad (4)$$

is not exactly zero as expected from a substrate which cannot solvolyse, i.e. benzyl bromide in acetone, but the k_{obs} values for [DMA] $\leqslant 0·15$ M drop successively down to the origin. The second-order rate constants, k_2 $(= k^f_{XY})$, were therefore determined using the slope of the plot of k_{obs} versus [DMA] higher than 0·15 *M* throughout in this work. The intercept appears to represent a very small portion of an S_N1 process concurrently proceeding with the dominant S_N2 reaction.[5] The drop in the k_{obs} values for DMA concentrations below *ca* 0·15 M could be due to ion-pair return;[5] the ion-pair intermediate formed in the S_N1 process can return to the original substrate if its lifetime is relatively short, before reacting with DMA in a fast step. When insufficient DMA molecules are available around the ion pair, as in the relatively dilute DMA solution (DMA $\leqslant 0·15$ M), the ion pair return process can compete with the nucleophilic attack by DMA in a fast step leading to a lower S_N1 rate constant, k_1. In the concentrated DMA solution, all the ion pairs can be captured during their lifetimes by the sufficient number of DMA nucleophiles in the immediate vicinity of the ion pair before returning to the substrate form. Notwithstanding this low level of S_N1 process possible, however, in most cases the k_1 value obtained from the intercept was small enough to be well within the experimental error of the k_2 determination (±3%), and hence was not pursued further.

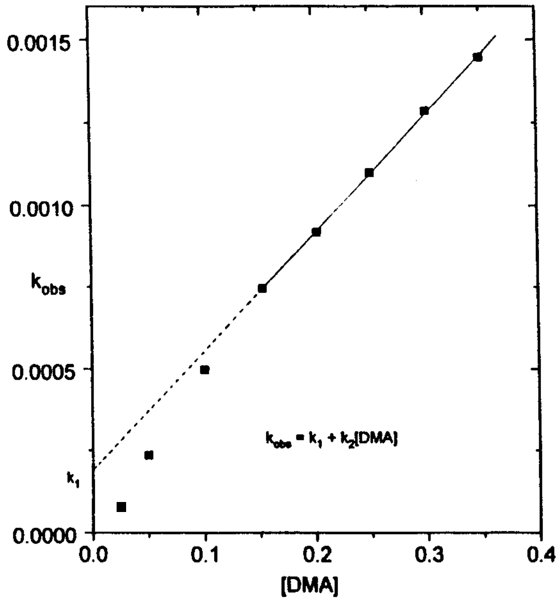

Figure 1. Plot of k_{obs} vs [DMA] for the reactions of Benzyl bromide ($Y = CH_3$) with *N,N*-dimethylaniline (X = H) in acetone at 45·0 °C

The k_2 $(= k^f_{XY})$ values for the forward reaction are summarized in Table 1 together with the two respective ρ values ρ_X and ρ^+_Y. In the case of the substrate substituent (Y) effect on log k_2, the use of the σ^+ value gave a better plot (ρ^+_Y). The rate is seen to be faster with a stronger nucleophile $(\delta\sigma_X < 0)$ and with a more electron-donating substituent in the substrate $(\delta\sigma^+_Y < 0)$. The latter trend suggests positive charge development at the benzylic carbon (C_α) in the TS; this is supported by the negative sign of ρ^+_Y. The extent of bond making in the TS increases with a more electron-withdrawing Y substituent, i.e. $\delta\rho_X < 0$ (or $\delta|\rho_X| > 0$) with $\delta\sigma^+_Y > 0$, and with a more electron-donating X substituent, i.e. $\delta\rho^+_Y > 0$ (or $\delta|\rho^+_Y| < 0$) with $\delta\sigma_X < 0$. These two trends reflect that ρ_{XY} is negative for the forward reaction series:[1]

$$\rho_{XY} = \frac{\partial^2 \log k_{XY}}{\partial\sigma_X\,\partial\sigma_Y} = \frac{\partial\rho_Y}{\partial\sigma_X} = \frac{\partial\rho_X}{\partial\sigma_Y} \quad (5)$$

The rate data in Table 1 were subjected to multiple regression analysis using equation (1) with $i, j = X, Y$, i.e. $k^f_{XY} = k_2$, and the ρ_{XY} value $(= -1·14)$ was determined:

$$\log(k^f_{XY}/k^f_{00}) = -0·97\sigma_X - 1·02\sigma^+_Y - 1·14\sigma_X\sigma^+_Y \quad (6)$$

as $-1·14$ $(r = 0·999)$; the sign is indeed negative with a relatively large magnitude.

In the reverse reaction, the k_{obs} value $(= k^r_{XY})$ was found to be independent of the concentration of benzylphenyldimethylammonium bromide salt (BAB) for [BAB] = $(1·00–4·20) \times 10^{-3}$ M with $k_{obs} = (1·02 \pm 0·03) \times 10^{-4}\,s^{-1}$. The k^r_{XY} values determined are given in Table 2 with the ρ_X values. The plot of log k^r_{XY} versus σ_Y exhibited a bent concave upward (U) curve, with a minimum rate shifting from Y = H to

Table 1. Rate constants [k_f (= k^f_{XY}) × 10^4 dm^3 mol^{-1} s^{-1}] for the forward reaction of benzyl bromide with *N*, *N*-dimethylaniline in acetone at 45·0 °C

	X					
Y	*p*-CH$_3$	*m*-CH$_3$	H	*p*-Br	*m*-Cl	ρ_X^{a}
p-CH$_3$	47·6	39·8	36·9	24·9	20·9	−0·67
m-CH$_3$	28·6	22·9	20·5	13·0	10·5	−0·82
H	24·9	20·0	18·1	10·4	8·32	−0·90
p-Cl	20·9	17·0	14·0	6·67	5·13	−1·19
m-Cl	11·5	8·71	7·28	3·53	2·24	−1·32
ρ^+_Y ^{a}	−0·90	−0·95	−1·04	−1·27	−1·45	

[a] Correlation coefficients were better than 0·996 in all cases.

Y = *m* − CH$_3$ as X is changed from an electron-donating to an electron-withdrawing group. This type of U-shaped Hammett plot has been attributed to a changing balance between the resonance and polar effects for different Y substituents in benzyl system;[6] the upward curvature in this plot for electron-withdrawing substituents occurs as a result of TS stabilization by electron withdrawal through the polar effect. The TS with electron-donating Y substituents are stabilized by a large resonance effect between the substituent and the benzene ring so that the rate becomes faster (see below).

The ρ_X values are positive, indicating that in the reverse reaction involving the decomposition of the quaternary ammonium salt (BAB), negative charge develops at the N atom of DMA.

The rate data (k^r_{XY}) in Table 2 were used to obtain the cross-interaction constant, ρ_{XY} (= +0·38), for the reverse process:

$$\log(k^r_{XY}/k^r_{00}) = 2{\cdot}24\sigma_x - 0{\cdot}18\sigma^+_Y + 0{\cdot}38\sigma_X\sigma^+_Y \quad (7)$$

(r = 0·992 except when Y = *m* − Cl).

It should be noted that for the forward process of bond making, the sign of ρ_{XY} is negative, but in contrast for the reverse process of bond cleavage, ρ_{XY} is positive. This sign change of ρ_{XY} from negative for a bond-making process to positive for a bond-breaking process appears to be a general trend. Our previous results indicated that in the normal S_N2 reactions, ρ_{XY} (bond-making process) is negative whereas ρ_{YZ} (bond-cleavage process) is positive in all cases.[1]

Table 2. Rate constants [k_r (= k^r_{XY}) × 10^4 s^{-1}] for the decomposition of benzylphenyldimethylammonium bromide in acetone at 45·0 °C

	X					
Y	*p*-CH$_3$	*m*-CH$_3$	H	*p*-Br	*m*Cl	ρ_X^{a}
p-CH$_3$	0·652	1·02	1·45	4·45	8·71	2·07
m-CH$_3$	0·473	0·759	0·953	3·42	7·08	2·16
H	0·428	0·708	1·02	3·55	7·59	2·29
p-Cl	0·557	0·955	1·25	4·36	8·71	2·19
m-Cl	0·692	1·12	1·48	4·79	9·33	2·11

[a] Correlation coefficients were better than 0·998.

The equilibrium constants, K_{XY}, calculated by k^f_{XY}/k^r_{XY} are given in Table 3. The K_{XY} values are greater with a more electron-donating X and also Y substituent, which is a reflection of a greater stability rendered to the product in the forward reaction, i.e. stabilization of the quaternary ammonium salt (BAB) by an electron-donating substituent in both the DMA and benzyl bromide. We subjected the equilibrium constants, K_{XY}, in Table 3 to multiple regression analysis using equation (1) (with K_{XY} rather than k_{XY}) and arrived at an equilibrium cross-interaction constant, ρ^e_{XY}, of −1·48:

$$\log(K_{XY}/K_{00}) = -3{\cdot}19\sigma_x - 0{\cdot}85\sigma^+_Y - 1{\cdot}48\sigma_X\sigma^+_Y \quad (8)$$

r = 0·995 excluding Y = *m* − Cl.

The equilibrium ρ values, ρ^e_X, ρ^{e+}_Y and ρ^e_{XY}, can also be determined using the relation $K_{XY} = k^f_{XY}/k^r_{XY}$; thus from equations (6) and (7), we obtain the derived values as in the equations

$$\rho^e_X = \rho^f_X - \rho^r_X = -0{\cdot}97 - 2{\cdot}24 = -3{\cdot}21 \quad (9a)$$

$$\rho^e_Y = \rho^f_Y - \rho^r_Y = -1{\cdot}02 - (-0{\cdot}18) = -0{\cdot}84 \quad (9b)$$

$$\rho^e_{XY} = \rho^f_{XY} - \rho^r_{XY} = -1{\cdot}14 - 0{\cdot}38 = -1{\cdot}52 \quad (9c)$$

The derived values in equations (9) compare well with those determined directly using the K_{XY} values in equation (8). The values directly determined in equation (8) and the derived values in equations (9) may not agree if the rate data used are not reliable and the

Table 3. Equilibrium constants [K_{XY}(dm^3 mol^{-1})] for the reaction of benzyl bromide with *N*, *N*-dimethylaniline in acetone at 45·0 °C

	X					
Y	*p*-CH$_3$	*m*-CH$_3$	H	*p*-Br	*m*-Cl	ρ^e_X^{a}
p-CH$_3$	73·0	39·0	25·4	5·60	2·40	−2·76
m-CH$_3$	60·5	30·2	21·5	3·80	1·48	−3·01
H	58·2	28·2	17·7	2·97	1·10	−3·22
p-Cl	36·2	17·8	11·1	1·53	0·589	−3·39
m-Cl	17·0	7·78	4·92	0·74	0·240	−3·44
ρ_Y^{b}	−0·75	−0·84	−0·90	−1·42	−1·52	

[a] Correlation coefficients ⩾ 0·996.

[b] Correlation coefficients ⩾ 0·988, excluding Y = *m*-Cl.

number of rate data is not sufficiently large, i.e. the correlations are not significant. This agreement lends credence to the ρ_{XY} values determined and applied as a mechanistic tool for organic reactions[1]. The following analysis shows that the equilibrium ρ_{XY} value, ρ^{e}_{XY}, reflects the intensity of interaction between the substituents X (σ_X) and Y (σ_Y) within a covalently bonded molecule, ρ^{COV}_{XY} (not in the TS for which the ordinary ρ_{XY}, an activation parameter, applies). To distinguish clearly an activation parameter, $\Delta\rho^{\ddagger}_{XY}$ ($\equiv \rho_{XY}$), from a state parameter, $\rho^{\ddagger}_{XY}$ or ρ^{0}_{XY}, we shall adopt the proper notations:[3]

$$\Delta\rho^{\ddagger}_{XY}\ (\equiv \rho_{XY}) = \rho^{\ddagger}_{XY} - \rho^{0}_{XY} \qquad (10a)$$

$$\Delta\rho^{\ddagger}_{YX}\ (\equiv \rho_{YX}) = \rho^{\ddagger}_{YX} - \rho^{0}_{YX} \qquad (10a)$$

$$\Delta\rho^{e}_{XY}\ (\equiv \rho^{e}_{XY}) = \Delta\rho^{\ddagger}_{XY}(\mathrm{f}) - \Delta\rho^{\ddagger}_{XY}(\mathrm{r}) = \Delta\rho^{\ddagger}_{XY} - \Delta\rho^{\ddagger}_{YX} \qquad (11)$$

where $\Delta\rho^{\ddagger}_{XY}(\mathrm{r}) = \Delta\rho^{\ddagger}_{YX}(\mathrm{f})$. Since $\rho^{0}_{XY} = 0$ (see above), $\rho^{0}_{YX} = \rho^{COV}_{YX}$ and by the principle of microscopic reversibility,[7] $\rho^{\ddagger}_{XY} = \rho^{\ddagger}_{YX}$, substitution of equations (10) into equation (11) and simplification leads to

$$\begin{aligned}\Delta\rho^{e}_{XY} &= (\rho^{\ddagger}_{XY} - \rho^{0}_{XY}) - (\rho^{\ddagger}_{YX} - \rho^{0}_{YX}) \\ &= \rho^{0}_{YX} = \rho^{COV}_{YX} = \rho^{COV}_{XY} \qquad (12)\end{aligned}$$

This analysis shows that the ρ^{e}_{XY} ($\equiv \Delta\rho^{e}_{XY}$) value obtained (−1·52) reflects the maximum intensity of interaction between the two substituents, X and Y, because ρ^{e}_{XY} is the intensity of interaction within a covalently bonded molecule,* not in the TS where the bond between the reaction centres of the nucleophile (X) and substrate (Y) is partially formed or broken leading to a weakening of the interaction between them.[3]

We can now normalize the ρ_X and ρ_{XY} values using ρ^{e}_{X} and ρ^{e}_{XY}, respectively, ($\rho^{n}_{X} = \rho_X/\rho^{e}_{X}$ and $\rho^{n}_{XY} = \rho_{XY}/\rho^{e}_{XY}$) as listed in Table 4.

Of course, we can also normalize the ρ_Y values in the same way but the normalized ρ_Y values have complexity owing to the non-linear ρ_Y plot found for the reverse process (see above) so that it is difficult to assess the proper meaning of the values.

Table 4. Normalized ρ_x and ρ_{XY} values

$\rho^{n}_{X}(\mathrm{f})$	$\rho^{n}_{X}(\mathrm{r})$	$\rho^{n}_{XY}(\mathrm{f})$	$\rho^{n}_{XY}(\mathrm{r})$
0·30	−0·70	0·77	−0·26

Since a DMA molecule reacts normally as a nucleophile in the present reaction series, the normalized values of ρ_X can be considered to reflect the fractional degree of charge development on N or the extent of the progress of reaction along the reaction coordinate as expressed solely by the polar interaction in the TS. Thus, in the forward reaction, bond formation has progressed *ca* 30% whereas in the reverse reaction the extent of bond cleavage is *ca* 70%. This is in good agreement with the generally accepted view of a relatively loose TS for such reactions[8] [equation (1)].

We note, however, that the normalized ρ_{XY} values do not agree with these extents of bond making and breaking in the TS based on the fractional change in polar interaction expressed as the normalized ρ_X values; since there can be no deprotonation or changes in the resonance interaction for the DMA in the TS, the normalized values of ρ_X reflect solely the fractional changes in polar interactions and hence are the true measure of the extent of the progress of reaction. This means that the magnitude of ρ^{n}_{XY} for the forward process is enhanced by 0·47 (=0·77 − 0·30) and that for the reverse process is depressed by −0·44 [= −0·70 − (−0·26)]; hence the inclusion of the effects of Y substituents which can resonance delocalize in the substrate leads us to conclude that in the forward and reverse processes the TS appears to be reached *ca* 45% too early and too late, respectively, along the reaction coordinate than the positions of the TS measured by the fractional changes in polar interactions alone. Although the difference between the solvation of DMA alone and that of the addition complex composed of the nucleophile and substrate may also contribute, the solvent effect will be small since the solvent used in this work (acetone) is relatively inert and weakly hydrogen bonding compared with water.[9]

This type of phenomenon is known to arise from an imbalanced TS[10] owing to a greater or lesser fractional loss of resonance than of polar interactions in the activation process for the reactions of carbenium ion with nucleophile (k_f) or of carbenium ion formation (k_r). Since the TS is a loose type, a substantial degree of positive charge development is expected at C_α. Also, as we noted in Figure 1, a possibility that an ion pair might be formed in a fast pre-equilibrium step and the nucleophilic attack on the carbenium ion of the tight ion-pair cannot be ruled out entirely. In such cases of the reactions of a well developed carbenium ion in a benzyl system at the TS, there is an imbalance or nonperfect synchronization between the development of resonance and polar interactions,[11] the lag in the development of resonance interactions for the formation of carbenium ion in the TS [k_r in equation (3)] corresponds to an early loss of resonance interactions in the TS for capture of carbenium ion by the nucleophile

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*Quantum mechanically, a covalent bond is that formed by sharing the electrons between atoms, and in this sense hydrogen molecule ion, H_2^+, is the simplest but the most important example of a molecule bound by a covalent bond. In contrast, an ionic bond is formed by electrostatic attraction between two charged atoms.

[k_f in equation (3)]. This sort of imbalanced TS has been observed for a number of reactions involving the formation and/or destruction of resonance-stabilized carbenium ions;[11,12] in our laboratory such cases have been noted for the reactions of 1-phenylethyl chlorides with methanol and aniline[13] and also, in a more intensified form, for the reactions of benzhydryl chlorides with anilines.[14] In these two examples, the magnitude of the ρ_{XY} value was large and the non-interactive phenomenon, in which at an observable σ_Y value, $\hat{\sigma}_Y$, ρ_X becomes zero and changes sign,[2,13,15] was observed. This balance of charge at N ($\rho_X = 0$) is possible since the proton transfer (deprotonation) from N of the aniline molecule is diffusion limited and hence may exceed in quantity the electronic charge transfer from N toward C_α in the N—C_α bond formation. In this work, however, no such non-interactive point was observable, since in the nucleophile DMA there is no proton to be transferred (or deprotonated) so that negative charge accumulation on N is not possible.

CONCLUSIONS

The reaction of benzyl bromide with DMA proceeds by a typical S_N2 process at DMA concentrations greater than *ca* 0·15 M; although only a very small portion of S_N1 channel was identified, it is within the range of experimental error and hence is insignificant in most cases. The reverse decomposition reaction of quaternary ammonium salt is pseudo-first order, the rate being independent of the salt concentration. The normalized value of ρ_X indicates that the progress of reaction as measured by the fractional change of polar interaction is *ca* 30% in the forward direction and *ca* 70% in the reverse direction, and hence the TS is relatively loose.

Comparison of the normalized ρ_X and ρ_{XY} values suggests that there is an imbalance or non-perfect synchronization between the fractional loss or development of resonance and polar interactions in benzyl system at the TS. In the forward reaction the fractional loss of resonance interaction becomes enhanced, whereas in the reverse reaction the fractional development of resonance interaction lags behind the corresponding changes in polar interaction by *ca* 45%.

The equilibrium cross-interaction constant, ρ^{e}_{XY}, represents a maximum intensity of interaction between substituents X and Y through covalent bonds within a molecule.

EXPERIMENTAL

Materials. Acetone was purified by the known method. *N*, *N*-Dimethylanilines were purified by distillation under reduced pressure or by recrystallization from water–acetone. Benzyl bromides from Aldrich (GR) were used as purchased. Benzylphenyldimethylammonium bromides were prepared by directly reacting benzyl bromides with *N*, *N*-dimethylanilines in ethanol under a nitrogen flow. After evaporation of ethanol, the products were recrystallized from ethanol–diethyl ether. The melting points and H^{1}NMR (250MHz) data are as follows.

p-CH$_3$-benzylphenyl-*p*-CH$_3$-dimethylammonium bromide: m.p. 145–148 °C; δ 6·9–7·7 (8H, m, aromatic), 5·6 (s, 2, CH$_2$), 3·9 (s, 6, N-CH$_3$), 2·3 (3H, s, Y-*p*-CH$_3$), 2·4 (3H, s, X-*p*-CH$_3$).

p-CH$_3$-benzylphenyl-*m*-CH$_3$-dimethylammonium bromide: m.p. 134–136 °C; δ 6·9–7·5 (8H, m, aromatic), 5·6 (2H, s, CH$_2$), 3·9 (6H, s, N-CH$_3$), 2·3 (3H, s, Y-*p*-CH$_3$), 2·4 (3H, s, X-*m*-CH$_3$).

p-CH$_3$-benzylphenyldimethylammonium bromide: m.p. 128–131 °C; δ 6·9–7·9 (9H, m, aromatic), 5·7 (2H, s, CH$_2$), 4·0 (6H, s, N-CH$_3$), 2·2 (3H, s, Y-*p*-CH$_3$).

p-CH$_3$-benzylphenyl-*p*-Br-dimethylammonium bromide: m.p. 136–138 °C; δ 6·9–7·9 (8H, m, aromatic), 5·7 (2H, s, CH$_2$), 4·0 (6H, s, N-CH$_3$), 2·3 (3H, s, Y-*p*-CH$_3$).

p-CH$_3$-benzylphenyl-*m*-Cl-dimethylammonium bromide: m.p. 138–140 °C; δ 6·9–7·8 (8H, m, aromatic), 5·7 (2H, s, CH$_2$), 4·0 (6H, s, N-CH$_3$), 2·3 (3H, s, Y-*p*-CH$_3$).

m-CH$_3$-benzylphenyl-*p*-CH$_3$-dimethylammonium bromide: m.p. 144–146 °C; δ 6·8–7·7 (8H, m, aromatic), 5·6 (2H, s, CH$_2$), 4·0 (6H, s, N-CH$_3$), 2·2 (3H, s, Y-*m*-CH$_3$), 2·4 (3H, s, X-*p*-CH$_3$).

m-CH$_3$-benzylphenyl-*m*-CH$_3$-dimethylammonium bromide: m.p. 146–148 °C; δ 6·8–7·6 (8H, m, aromatic), 5·6 (2H, s, CH$_2$), 4·0 (6H, s, N-CH$_3$), 2·2 (3H, s, Y-*m*-CH$_3$), 2·4 (3H, s, X-*m*-CH$_3$).

m-CH$_3$-benzylphenyldimethylammonium bromide: m.p. 149–151 °C; δ 6·8–7·8 (9H, m, aromatic), 5·6 (2H, s, CH$_2$), 4·0 (6H, s, N-CH$_3$), 2·2 (3H, s, Y-*m*-CH$_3$).

m-CH$_3$-benzylphenyl-*p*-Br-dimethylammonium bromide: m.p. 158–160 °C; δ 6·8–7·8 (8H, m, aromatic), 5·7 (2H, s, CH$_2$), 4·0 (6H, s, N-CH$_3$), 2·2 (3H, s, Y-*m*-CH$_3$).

m-CH$_3$-benzylphenyl-*m*-Cl-dimethylammonium bromide: m.p. 156–158 °C; δ 6·8–7·6 (8H, m, aromatic), 5·7 (2H, s, CH$_2$), 4·0 (6H, s, N-CH$_3$), 2·2 (3H, s, Y-*m*-CH$_3$).

Benzylphenyl-*p*-CH$_3$-dimethylammonium bromide: m.p. 150–152 °C; δ 7·0–7·7 (9H, m, aromatic), 5·7 (2H, s, CH$_2$), 4·0 (6H, s, N-CH$_3$), 2·4 (3H, s, X-*p*-CH$_3$).

Benzylphenyl-*m*-CH$_3$-dimethylammonium bromide: m.p. 154–156 °C; δ 6·8–7·6 (9H, m, aromatic), 5·6 (2H, s, CH$_2$, 3·9 (6H, s, N-CH$_3$), 2·4 (3H, s, X-*m*-CH$_3$).

Benzylphenyldimethylammonium bromide: m.p. 156–158 °C; δ 7·0–7·7 (10H, m, aromatic), 5·6 (2H, s, CH$_2$), 3·9 (6H, s, N-CH$_3$).

Benzylphenyl-*p*-Br-dimethylammonium bromide: m.p. 164–166 °C; δ 7·1–7·8 (9H, m, aromatic), 5·6 (2H, s, CH_2), 3·9 (6H, s, N-CH_3).

Benzylphenyl-*m*-Cl-dimethylammonium bromide: m.p. 170–172 °C; δ 7·1–7·6 (9H, m, aromatic), 5·7 (2H, s, CH_2), 4·0 (6H, s, N-CH_3).

p-Cl-benzylphenyl-*p*-CH_3-dimethylammonium bromide: m.p. 146–148 °C; δ 7·2–7·9 (8H, m, aromatic), 5·7 (2H, s, CH_2), 3·9 (6H, s, N-CH_3), 2·4 (3H, s, X-*p*-CH_3).

p-Cl-benzylphenyl-*m*-CH_3-dimethylammonium bromide: m.p. 145–147 °C; δ 7·1–7·7 (8H, m, aromatic), 5·7 (2H, s, CH_2), 4·0 (6H, s, N-CH_3), 2·4 (3H, s, X-*m*-CH_3).

p-Cl-benzylphenyldimethylammonium bromide: m.p. 147–148 °C; δ 7·3–7·9 (9H, m, aromatic), 5·7 (2H, s, CH_2), 4·0 (6H, s, N-CH_3).

p-Cl-benzylphenyl-*p*-Br-dimethylammonium bromide: m.p. 150–152 °C; δ 7·3–7·7 (8H, m, aromatic), 5·7 (2H, s, CH_2), 3·9 (6H, s, N-CH_3).

p-Cl-benzylphenyl-*m*-Cl-dimethylammonium bromide: m.p. 154–156 °C; δ 7·2–7·6 (8H, m, aromatic), 5·7 (2H, s, CH_2), 4·0 (6H, s, N-CH_3).

m-Cl-benzylphenyl-*p*-CH_3-dimethylammonium bromide: m.p. 146–148 °C; δ 7·2–7·8 (8H, m, aromatic), 5·7 (2H, s, CH_2), 3·9 (6H, s, N-CH_3), 2·4 (3H, s, X-*p*-CH_3).

m-Cl-benzylphenyl-*m*-CH_3-dimethylammonium bromide: m.p. 144–146 °C; δ 7·2–7·8 (8H, m, aromatic), 5·7 (2H, s, CH_2), 3·9 (6H, s, N-CH_3), 2·4 (3H, s, X-*m*-CH_3).

m-Cl-benzylphenyldimethylammonium bromides: m.p. 147–150 °C; δ 7·3–7·7 (9H, m, aromatic), 5·7 (2H, s, CH_2), 4·0 (6H, s, N-CH_3).

m-Cl-benzylphenyl-*p*-Br-dimethylammonium bromide: m.p. 152–155 °C; δ 7·3–7·7 (8H, m, aromatic), 5·7 (2H, s, CH_2), 4·0 (6H, s, N-CH_3).

m-Cl-benzylphenyl-*m*-Cl-dimethylammonium bromide: m.p. 154–156 °C; δ 7·3–7·7 (8H, m, aromatic), 5·7 (2H, s, CH_2), 4·0 (6H, s, N-CH_3).

Kinetic methods. Rates were measured conductimetrically at 45·0 ± 0·05 °C in acetone. Pseudo-first-order rate constants, k_{obs}, were determined by the Kezdy–Swinbourne method[16] with a large excess of DMA, more than 500-fold of the substrate concentration. Second-order rate constants, k_2, were obtained from equation (4). The rate constant for the reverse reaction k_{obs}, was independent of the quaternary ammonium salt concentration so that the k_{obs} values are reported.

Product analysis. In both directions of the reaction, after reacting at least ten half-lifes under the same kinetic conditions, three species, benzyl bromide, DMA and quaternary ammonium salt, were confirmed by TLC analysis. No other species was detected.

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