The Influence of the Solvent on Reaction Velocity

XXXVII. Benzoylation of Anilines in Different Solvents

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The reactions of benzoyl chloride with aniline, *p*-chloroaniline, *m*-nitroaniline, and *p*-nitroaniline have been studied in benzene, diethyl ether, and five benzene-ether mixtures. In each case the rate constant increases with the proportion of ether until the ether percentage becomes greater than 50, after which there occurs a slight decrease. E and A fall steeply up to an ether content of about 10 % and then pass through a flat minimum. The reaction of benzoyl chloride with aniline was investigated also in three benzene-acetone mixtures. Already very small amounts of acetone accelerate the reaction greatly, by causing a steep fall in E, and also A falls steeply. The low values of E and A and the influence of the solvent on them are discussed. The isodielectric activation energies and frequency factors decrease with increasing dielectric constant of the solvent. The plots of log A_ε vs. E_ε are linear, whereas the plots of the iso-composition values are not. The Hammett reaction parameter ϱ is negative and a linear function of $1/T$ at constant ε, but the plot of ϱ vs. $1/\varepsilon$ at constant T passes through a maximum. The substituent effects are dependent on the solvent and on the temperature. The influence of the non-electrostatic term on the ratio k_s/k_u is in general greater than that of the electrostatic term.

In a recent paper [1] of this series, it was shown that the substituent effects in the reaction

$$X + C\overset{r_0}{-\!\!\!-\!\!\!-}Y \longrightarrow X\overset{r_1}{-\!\!\!-\!\!\!-}C\overset{r_2}{-\!\!\!-\!\!\!-}Y \longrightarrow \text{products}$$
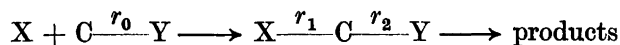
where C is the centre of the reaction, usually a carbon atom, can in general with good approximation be expressed by the equation

$$\ln \frac{k_s}{k_u} = -\frac{e_X \delta e_C}{RT r_1} + \frac{e_Y \delta e_C}{RT}\left[\frac{1}{r_0} - \frac{1}{r_2}\right] - \frac{\Delta W}{RT} \tag{1}$$

where

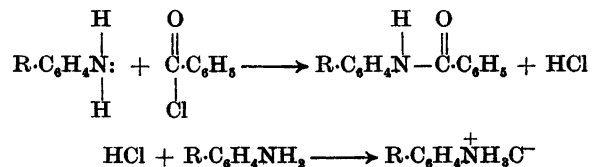|	
k_s	= the rate constant of the substituted compound
k_u	= the rate constant of the unsubstituted compound
e_X, e_Y and e_C	= the effective electric charges of the attacking reagent X, the leaving atom or group Y, and the atom in the reaction centre, respectively
δe_C	= the increment, positive or negative, caused to the charge e_C by the substituent introduced in the substrate molecule
r_0	= the distance C—Y in the unperturbed (substituted) substrate molecule
r_1 and r_2	= the distances X—C and C—Y in the transition state
ε	= the dielectric constant of the solvent
ε'	= a quantity that is connected with the internal dielectric constant of the substrate and with the medium in which the substrate is situated
$\Delta W/RT$	= the non-electrostatic part of ln (k_s/k_u).

If the effective charge of the attacking reagent X is changed, *e.g.* by introducing a substituent, but the substrate molecule is not changed, the equation simplifies to

$$\ln \frac{k_s}{k_u} = -\frac{e_C \delta e_X}{RT r_1} - \frac{\Delta W}{RT} \qquad (2)$$

where δe_X is the increment in the charge of X.

According to these equations the substituent effects should be dependent on the dielectric constant of the medium and on the temperature. Eqn. (1) has been tested with good success on a great number of organic reactions in binary solvent systems whose compositions were varied.[1] Abundant experimental data are available for reactions in mixtures of various organic liquids and water or alcohols, but published data on reactions in non-hydroxylic solvents are limited to reactions between pyridines and methyl iodide in benzene-nitromethane mixtures[2] and to the benzoylation of anilines in various solvents.[3-5] Both of these series of reactions are of the type where the charge of the attacking reagent is changed and thus afford data to test the validity of eqn. (2).

Since further studies of the benzoylation of anilines seemed to be of considerable interest from the standpoint of the above theory, we have carried out a kinetic investigation of the reaction

$$\text{R·C}_6\text{H}_4\overset{\text{H}}{\underset{\text{H}}{\text{N}}}: + \overset{\text{O}}{\underset{\text{Cl}}{\text{C·C}_6\text{H}_5}} \longrightarrow \text{R·C}_6\text{H}_4\overset{\text{H}}{\text{N}}-\overset{\text{O}}{\text{C·C}_6\text{H}_5} + \text{HCl}$$

$$\text{HCl} + \text{R·C}_6\text{H}_4\text{NH}_2 \longrightarrow \text{R·C}_6\text{H}_4\overset{+}{\text{NH}_3}\text{Cl}^-$$

in some pure liquids and in diethyl ether-benzene and benzene-acetone mixtures. It may be mentioned that there are considerable restrictions in the choice of the solvents. The reactions are too fast in some solvents, and, on

the other hand, although the reactions are slower in aliphatic hydrocarbons and in carbon tetrachloride, they are influenced markedly by the separated solid particles of the reaction products.[3a] As benzoyl chloride reacts with hydroxylic solvents and dimethyl sulphoxide, these solvents are excluded. Diethyl ether was chosen as a solvent component together with benzene although its dielectric constant is not much higher than that of benzene, partly for the sake of convenience, but also because it was difficult to find other solvent systems where the reactions could be followed without great difficulties over the whole range of mixtures. It was also of certain interest that a solvent as common as ether has only seldom been used as a medium in chemical kinetics. The benzoylation of aniline was studied also in three benzene-acetone mixtures.

EXPERIMENTAL

Chemicals. Aniline (Fluka AG, *puriss.*) was distilled twice at reduced pressure. Benzoyl chloride (Fluka AG, *pro analysi*), *p*-chloroaniline and *p*-nitroaniline (Fluka AG, *puriss.*) were used as received. *m*-Nitroaniline (Fluka AG, *purum*) was crystallized from water; it then melted at 113—114°.

Benzene (Fluka AG, *pro analysi*) was used as received except for some runs in the pure solvent for which it was dried with sodium and distilled. Ether was dried with sodium and distilled. Baker's Analyzed acetone was dried with potassium carbonate and distilled.

Method. According to eqn. (3), one mole of anilinium chloride corresponds to one mole of benzoyl chloride and two moles of aniline. In the experiments with unsubstituted aniline, equal volumes (20 ml) of a 0.01 M solution of benzoyl chloride and a 0.02 M solution of aniline were pipetted into two-compartment reaction vessels described previously [6] and mixed together after thermostating. The initial concentrations of the reactants after mixing were thus: benzoyl chloride 0.005 M, aniline 0.01 M. At suitable intervals, the reaction was stopped by adding 50 ml of light petroleum (b.p. 62—82°) to a reaction vessel. Anilinium chloride was extracted from this solution as quickly as possible with 50 ml of cold water in a separatory funnel. The light petroleum also retarded the simultaneous hydrolysis of benzoyl chloride. The water extract was then analyzed for chloride ion by potentiometric titration with 0.02 N silver nitrate solution. The experiments with *p*-chloroaniline were carried out starting with solutions of the same initial concentrations, but using 10-ml amounts of each solution; in these cases 0.01 N silver nitrate was used as titrant.

The reactions of the nitroanilines are slow and were therefore carried out in sealed ampoules of Pyrex glass to each of which 10 ml of a solution 0.01 M in benzoyl chloride and 0.02 M in aniline was added. The reactions were stopped with light petroleum and the anilinium chloride was extracted with water as above and titrated with 0.01 N silver nitrate.

The titrations were carried out using a Radiometer 22 pH-meter, a silver chloride electrode, and a mercurous sulphate electrode, type K 601, as reference electrode. The potential jump at the equivalent point is rather small and therefore 2 ml of 6 N acetic acid was added to the sample and the resulting solution was cooled in ice-water before the titration, during which the solution was shielded from light.

The solvent mixtures used in the kinetic experiments were prepared by mixing weighed volumes of the components.

The temperatures of the water thermostats remained constant within ±0.02°. The experiments at 0° were carried out in a well-insulated vessel which contained crushed ice and water. For —10°, a low-temperature thermostat was used; the temperature could be controlled to within ±0.05°. The thermometers of the thermostats were checked against a thermometer certified by the National Bureau of Standards (U.S.A.).

The rate constants of the reactions were computed from the equation

$$k = \frac{100}{2at} \left[\frac{1}{100-p} - \frac{1}{100} \right]$$

Table 1. Some typical runs. B=benzoyl chloride.

Aniline+B in benzene at 40° a=0.005			p-Chloroaniline+B in 40 vol-% ether-benzene-mixture at 15°, a=0.005			m-Nitroaniline+B in 10 vol-% ether-benzene-mixture at 50°, a=0.01		
t, min.	p	100k	t, min.	p	100k	t, min.	p	100k
5	26.0	11.7	20	25.2	2.81	125	26.1	0.236
8	35.0	11.2	25	30.2	2.88	150	29.8	0.236
10	41.1	11.6	30	33.2	2.76	195	36.1	0.241
12	45.2	11.5	40	40.2	2.80	245	39.0	0.220
15	49.8	11.0	50	45.5	2.78	270	42.7	0.230
18	54.8	11.2	60	50.3	2.81	290	43.4	0.220
20	57.4	11.2	80	57.0	2.76	305	44.8	0.222
						1132	73.3	0.202

where a is the initial concentration of benzoyl chloride and p is the change in per cent. The number of samples analysed in each run was seven or eight. The results of three typical runs are recorded in Table 1. Because the rate constants were somewhat dependent on the initial concentrations,[3b] experiments with each aniline were always made using the same initial concentration.

RESULTS AND DISCUSSION

1. Rate constants and activation parameters in mixed solvents. The compositions of the benzene-ether mixtures used as solvents were:

Ether, vol-%	0	10	20	40	60	80	100
» wt.-%	0	8.2	16.6	34.7	54.4	75.9	100
» mole-%	0	8.6	17.3	35.9	55.7	76.8	100

The results of the kinetic measurements are summarised in Tables 2—5. The activation energies, E, and frequency factors, A (in l mole^{-1} sec^{-1}), were calculated from the rate constants at different temperatures by the method

Table 2. The reaction between aniline and benzoyl chloride in benzene-ether mixtures. $a=0.005$.

Ether, wt.-%	100k, l mole^{-1} sec^{-1}					E cal	log A	ΔS* (25°)	ΔG* cal
	−10.00°	0.00°	15.00°	20.00°	25.00°				
0			3.82		6.27[b]	7 970	4.635	−39.3	19 095
8.2		3.57	6.32	7.69	9.34	6 170	3.492	−44.5	18 860
16.6		4.59	8.28	9.88	11.7	6 060	3.520	−44.4	18 700
34.7	4.14[a]	6.16	10.9		15.4	5 960	3.558	−44.2	18 560
54.4	4.40	6.73	11.7		16.7	5 900	3.550	−44.3	18 510
75.9	4.38	6.48	11.9		16.7	6 010	3.633	−43.9	18 510
100	4.22	6.20	11.2		16.3	6 140	3.709	−43.5	18 530

[a] At −9.50°. [b] At 40° 100k=11.6.

Table 3. The reaction between *p*-chloroaniline and benzoyl chloride in benzene-diethyl ether mixtures. $a = 0.005$.

Ether, wt.-%	$100k$, l mole^{-1} sec^{-1}					E cal	$\log A$	ΔS^* (25°)	ΔG^* cal
	0.00°	15.00°	20.00°	25.00°	40.00°				
0	a	0.869		1.31	2.60	7 690	3.770	−43.3	19 990
8.2	0.863	1.57	1.93	2.32		6 400	3.055	−46.5	19 680
16.6	1.19	2.10	2.51	3.05		6 070	2.931	−47.1	19 520
34.7	1.58	2.78		4.16		6 210	3.168	−46.0	19 340
54.4	1.60	2.95		4.24		6 310	3.257	−45.6	19 320
75.9	1.51		3.43	4.14		6 510	3.393	−45.0	19 340
100	1.25^b	2.41		3.69		6 880	3.609	−44.0	19 410

^{a} At 7.50° $100k = 0.619$; ^{b} at −10.20° $100k = 0.777$.

of least squares, the plots of log k against $1/T$ being linear within the limits of experimental error in all cases. The entropy of activation, ΔS^*, was computed for 25° from the formula $A = 2(kT/h)\exp\Delta S^*/R$, and the free enthalpy of activation, ΔG, from the equation $\Delta G^* = E - RT - T\Delta S^*$. All rate constants were corrected for the thermal expansion of the solvent using correction factors (Table 6) obtained by interpolation from the density data given in Timmerman's book.[7]

It is seen from the tables that addition of ether to benzene increases the reaction rate at first, but at higher ether concentrations the reaction rate decreases slightly. At both ends of the solvent mixture series, the changes in the reaction velocities are determined by changes in the activation energies which outweigh the opposite effects of the changes in the frequency factor. In the middle range of the mixtures, the changes in the frequency factor determine the situation. The plots of log A against E consist of two approximately linear parts (Fig. 1), as often is the case. The values k, E, and log A for the reactions in benzene are in good agreement with the data of Hinshel-

Table 4. The reaction between *m*-nitroaniline and benzoyl chloride in benzene-diethyl ether mixtures. $a = 0.01$.

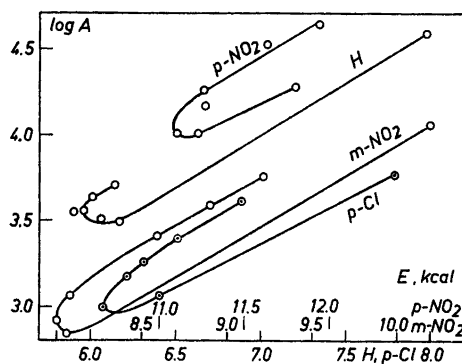| Ether, wt.-%	10^4k, l mole^{-1} sec^{-1}				E cal	$\log A$	ΔS^* (25°)	ΔG^* cal
	25.00°	40.00°	50.00°	60.00°				
0	3.78	9.33	13.7	23.9	10 200	4.061	−41.9	22 110
8.2	8.66	15.9	23.5	36.7	8 060	2.837	−47.5	21 540
16.6	11.0	20.8	31.6	45.4	8 000	2.911	−47.2	21 480
34.7	13.5	25.9	37.6	57.5	8 080	3.056	−46.5	21 360
54.4	13.0	25.6	39.2	59.8	8 590	3.410	−44.9	21 390
75.9	11.6	23.1	37.3	55.9	8 900	3.587	−44.1	21 460
100	10.1	21.2	33.1	52.1	9 210	3.756	−43.3	21 540

Fig. 1. Benzene-diethyl ether mixtures. Plot of log A against E.

wood and his collaborators,[3] especially if we take into account that their rate constants were not corrected for the thermal expansion of the solvent (*cf.* also Refs. 4 and 5). All the substituents in the compounds studied are electron-attracting. They cause the lone electron pair of the nitrogen atom of the —NH_2 group to be held more tightly and thus retard the reaction. Electron-

Table 5. The reaction between *p*-nitroaniline and benzoyl chloride in benzene-diethyl ether mixtures. $a = 0.01$.

Ether, wt.-%	$10^4 k$, 1 mole^{-1} sec^{-1}				E cal	log A	ΔS^* (25°)	ΔG^* cal
	25.00°	40.00°	50.00°	60.00°				
0 [a]	0.421	1.10			11 800	4.277	—40.9	23 420
8.2	0.609	1.43	2.58	4.45	11 230	4.011	—42.2	23 210
16.6	0.769	1.72	3.15	5.49	11 100	4.010	—42.2	23 080
34.7		2.06	3.76	6.16	11 260	4.261	—41.0	22 900
54.4	0.794		3.61	5.75	11 270	4.165	—41.5	23 030
75.9		1.80	3.14	5.59	11 630	4.524	—39.8	22 910
100		1.45	2.62	4.64	11 940	4.665	—39.2	23 020

[a] Ref. 3b.

Table 6. Temperature expansion coefficients of benzene-diethyl ether mixtures.

Ether, wt.-%	—10°	0°	15°	20°	25°	40°	50°	60°
0			0.995	1.000	1.005	1.025	1.038	1.052
8.2		0.976	0.994	1.000	1.006	1.026	1.039	1.053
16.6		0.975	0.993	1.000	1.007	1.027	1.041	1.055
34.7	0.962	0.973	0.993	1.000	1.006	1.027	1.042	1.056
54.4	0.960	0.973	0.993	1.000	1.007	1.028	1.044	1.059
75.9	0.953	0.968	0.992	1.000	1.008	1.034	1.052	1.071
100	0.955	0.969	0.993	1.000	1.008	1.033	1.050	1.069

Table 7. The reaction between aniline and benzoyl chloride in benzene-acetone mixtures.
$a = 0.005$.

Ace- tone, wt.-%	$100k$, 1 mole^{-1} sec^{-1}					E cal	$\log A$	ΔS^* (25°)	ΔG^* cal
	0.00°	7.05°	15.00°	25.00°	40.00°				
0			3.82	6.27	11.6	7 970	4.635	−39.3	19 095
1.0		6.31	8.02	11.2	18.8	5 930	3.419	−44.9	18 730
9.2	34.2	37.1	44.3	63.1		3 980	2.698	−48.4	17 760
18.5	58.6[a]		67.4	72.4		1 320	0.855	−56.6	17 600

[a] At −9.90° $100k = 54.3$.

repelling substituents in the amine would have an opposite effect. Conversely, electron-attracting substituents in the acid chloride increase and electron-repelling substituents decrease the reaction velocity.[3] Accordingly, the observed substituent effects are consistent with the assumption that the variation of the repulsion between the reactants is the principal factor determining the changes in the reaction velocities.

Very striking, however, are the low values of the activation energies and the highly negative activation entropies and the fact that the activation entropy does vary much from compound to compound. The problem has been discussed by Hinshelwood over and over again and very little can be added to his conclusions.

The low activation energies are easy to understand, for it is clear that the repulsion between the nitrogen atom of the $-NH_2$ group and the carbon atom of the $-COCl$ group cannot be large because the former, owing to its lone electron pair, is electrically negative, and the latter, due to the influences of the oxygen atom and the chlorine atom, positively charged. A corresponding situation prevails in the formation of quaternary ammonium salts,[2,8] but the activation energy is for these reactions greater because the carbon atom at the seat of reaction is less positive.

The activation entropies are highly negative also in the formation of quaternary ammonium salts. They have been discussed on the basis of statistical theory [8] to which also Hinshelwood has drawn attention in his work on the benzoylation of amines. According to this theory,[9] if the reactants are non-linear polyatomic molecules, the frequency factor

$$A = \frac{kT}{h} \times \frac{q_v^5}{q_t^3 q_r^3}$$

where q_v, q_t, and q_r are the vibrational, translational, and rotational partition functions for one degree of freedom of each type. The collision number Z is approximately equal to $(kT/h)(q_r^2/q_t^3)$ and hence the probability factor P of the collision theory, defined by $A = PZ$, is

$$P = (q_v/q_r)^5$$

At ordinary temperatures q_v differs only little from unity, but q_r can have values from 10 to 100, so that P should be of the order of $10^{-5}-10^{-10}$ for reactions of polyatomic molecules. This is so only for gas reactions; for reactions in solution, the solvent modifies the partition functions in a way that is not accurately known, and, accordingly, the calculations are more uncertain. The collision frequency Z is about 2.8×10^{11} also for reactions in solution [10] at $25°$ and thus experimental values of log A from 3 to 4 correspond to values of P from 3×10^{-9} to 3×10^{-10}.

Hinshelwood has also pointed out that there will be a considerably greater charge separation in the transition state,

$$\underset{\underset{H}{|}}{RC_6H_4-N}\cdots\overset{\overset{O}{\|}}{\underset{\underset{Cl}{|}}{C}}-C_6H_4$$
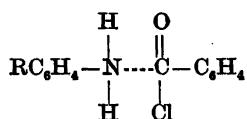
than in the reactant molecules separately, wherefore the transition complex will orient more solvent molecules than both reactants together. The influence of increasing polarity of the medium on such reactions is well known: E and A are both lowered. Yet it is important to note, that the values of A for reactions in different pure solvents are of the same order of magnitude. For instance the following results have been reported for the reaction between aniline and methyl chloride:

Solvent	benzene	carbon tetrachloride	nitrobenzene	acetone	ether
log A	4.64[a]	3.60[b]	4.63[c]	4.85[c]	3.7[a]

[a] Table 3. [b] Ref. 3a. [c] Ref. 5.

Of these solvents, carbon tetrachloride is non-polar and fully symmetrical and, therefore, its molecules do not undergo any orientation around the transition complex. In addition, there is no reason to believe that its molecules would have a greater attraction for the transition complex than for the reactants. Nitrobenzene is strongly polar and, accordingly, greatly oriented by the transition complex. Ether is less polar. Benzene is non-polar, but owing to its π-electrons, it is oriented by strongly polar molecules.[11,12] These results show that the influence of the differences in the solvation of the transition state and the reactants by pure solvents must be relatively small or that there are specific solvent effects that counteract them.

Tables 2—5 show that addition of up to 10 % ether to benzene lowers the activation energy by 1300—2200 cal and the frequency factor by about one power of ten, except in the case of p-nitroaniline where the changes are smaller. At higher ether contents E and A change only slightly. Quite drastic lowerings in the values of E and A are caused by acetone (Table 7), and very marked lowerings also by nitrobenzene [3h] and phenyl cyanide.[3h] The fall of E and A may well be due to a gradual increase in the solvation of the transition complex as more molecules of the polar solvent become available, as

already pointed out by Hinshelwood.[3h] When there are enough polar molecules to surround the complex, E and A will not undergo much further change. To explain the increase of E and A on further addition of the polar solvent at high concentrations, various factors can be invoked. The solvent may prevent the relapse of the transition complex to its original state.[8] Also the internal structure of the solvent may be of importance. Pearson [13] has pointed out that the molecules in a strongly polar solvent already exist in a partially "frozen" state because of strong intermolecular forces, whereas the molecules in non-polar liquids are free. Hence, when they become bound to the reactants or the transition state, the molecules of a strongly polar solvent suffer only a relative small loss of entropy. On the other hand, the heat of solvation is reduced by the work required to loosen molecules of the solvent from the structure of the bulk liquid. The fact that further addition of the polar solvent component finally increases the energy of activation might now be explained by a simultaneous increase of the above work. The increase of A at high concentrations of the polar component also explains why the values of A are of the same order of magnitude in all solvents.

According to Ingold,[14] reactions in which the transition state is more polar than the reactant molecules separately should be experience a rate increase on going to a more polar solvent. Although the results obtained do not show any general unambiguous relationship between the rate constant and the dipole moment of the solvent, a rough correlation in the sense of the theory can be seen. Especially the strongly polar solvents nitrobenzene, benzonitrile, and acetone accelerate the reaction powerfully as is seen from Tables 2—5 and 7 and the results of Hinshelwood.[3f,h] Ingold has, however, pointed out that the polarity of the solvent increases with the dipole moment, but that it decreases with increased thickness of shielding of the dipole charges.

Soper et al.[15] have suggested that the solvent tends to disrupt the critical complex into those substances for which the solvent has the greater affinity. Here this means that a more polar solvent favours the disruption of the transition state to the reaction products more than a less polar solvent.

The transition state in the reaction between benzoyl chloride and aniline has been discussed also by Elliot and Mason [16] and Mather and Shorter.[17]

2. *Reaction rate and the dielectric constant of the solvent.* According to dielectric theory, we have for a reaction between two dipoles [1]

$$\ln k = \ln k_0 - \frac{e_X e_C}{RT r_1} \frac{1}{\varepsilon} + \frac{\Delta W}{RT} + \text{const.} \tag{3}$$

or [18]

$$\ln k = \ln k_0 + \frac{3}{8kT} \left(\frac{2}{\varepsilon} - 1 \right) \left[\frac{\mu_A^2}{r_A^3} + \frac{\mu_B^2}{r_B^3} - \frac{\mu_*^2}{r_*^3} \right] \tag{4}$$

where k_0 is the rate constant in the standard solvent and the μ's and r's are the dipole moments and the radii of the reactant molecules A and B and the transition complex. Eqn. (3) implies since $-e_X e_C$ is positive for the reactions in question, that $\ln k$ should increase linearly with the reciprocal of the dielectric constant if ΔW is constant or can be neglected. The same result is obtained from eqn. (4) if the term μ_*^2/r_*^3 is smaller than the sum of the other
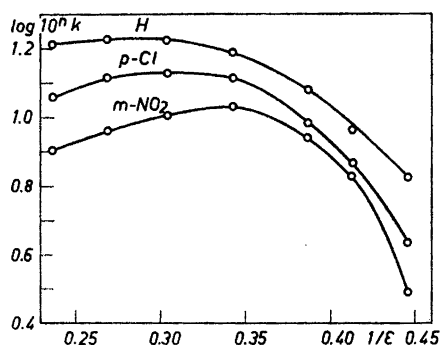
Fig. 2. Plot of log k against the reciprocal of the dielectric constant, temperature 25°.

two terms, which might well be possible even when μ_* is large, because the radius of the transition complex, r_*, will always be greater than the radii of the reactant molecules. Too much emphasis need not be placed on the linearity of the plot, since the relative importance of the terms may change with the solvent. The plots obtained for the studied reactions in ethyl ether-benzene mixtures are represented in Fig. 2. There is a slight increase of log k up to about 40 % benzene, but further addition of benzene decreases the reaction rate. Probably the term $\Delta W/RT$, which includes the solvation effects, decreases gradually with increasing proportion of the less polar solvent, benzene. This is equivalent to a simultaneous decrease of r_* and a corresponding increase of μ_*^2/r_*^3. In nitrobenzene-benzene mixtures log k decreases continuously with increasing proportion of benzene.[3h]

The points log k, $1/\varepsilon$ for the reactions in various pure solvents are very scattered, but in general the rate constant is greater the greater the dielectric constant of the solvent.[1,3f,e,h,5] Thus the important role of solvation phenomenon manifests itself here, too.

3. Isodielectric solvents. The rate constants for isodielectric ethyl ether-benzene mixtures were determined from the isocomposition values given in Tables 2—5 by the usual graphical interpolation method. They obey the Arrhenius equation very satisfactorily. The isodielectric activation energies, E_ε, and frequency factors, A_ε, which deviate relatively little from the isocomposition parameters, decrease with increasing dielectric constant (Table 8).

Table 8. Isodielectric benzene-diethyl ether mixtures.

ε	H		p-Cl		m-NO$_2$		p-NO$_2$	
	E	$\log A$	E	$\log A$	E	$\log A$	E	$\log A$
2.50	7 390	4.448	7 750	4.115	9.480	3.946	12.310	4.867
3.00	6 420	3.970	6 640	3.479	8 310	3.321	11 750	4.625
3.50	6 000	3.623	6 250	3.204	8 090	3.024	11 290	4.295
4.00	5 880	3.524	6 020	3.106	8 260	3.079	10 610	3.718

Fig. 3. Plot of log A_ε against E_ε.
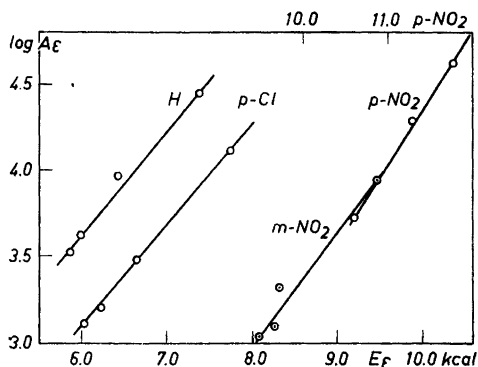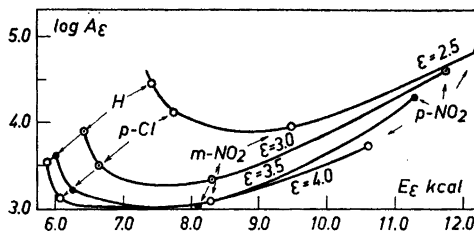
Fig. 4. Plot of log A_ε against E_ε for different compounds.

It is remarkable that the plots of log A_ε against E_ε are straight lines (Fig. 3), and thus differ from the plots of the isocomposition values (Fig. 1). The plots of log A_ε against E_ε of different compounds (Fig. 4) are similar in form to the corresponding isocomposition plots, but more regular.

The dielectric constants of benzene-ether mixtures (Table 9) were measured using the Dipolmeter Type DM 01 of the Wissenschaftlich-technische Werkstätten, Weilheim, Oberbayern, West-Germany.

4. Substituent effects and the solvent. Since the substituents are all in aniline, *i.e.* in the attacking reagent, their effects should follow eqn. (2). All substituents in the compounds studied in the present work are electron-attracting, and, as already mentioned, such substituents cause the lone electron pair on the nitrogen atom in the group $-NH_2$ to be bound more tightly. Thus the increment δe_x is positive, and as e_C also is positive, the product $e_\text{C}\delta e_\text{x}$ is positive, and if the term $-e_\text{C}\delta e_\text{x}/RTr_1$ is greater than the term $\Delta W/RT$, ln (k_s/k_u) should be negative or $k_s/k_u < 1$, which is in accordance with the experimental results. Furthermore, the more the substituent attracts electrons, the greater is δe_x and the smaller k_s/k_u.

Eqn. (2) implies also that the ratio k_s/k_u should be dependent on the dielectric constant of the solvent and on the temperature. If ΔW remains

Table 9. Dielectric constants of benzene-diethyl ether mixtures.

t	Ether, wt.-%						
	0	8.2	16.6	34.7	54.4	75.9	100
0°C	2.34	2.52	2.71	3.11	3.56	4.09	4.74
15	2.29	2.46	2.63	2.99	3.40	3.86	4.42
25	2.26	2.42	2.58	2.92	3.29	3.71	4.22
30	2.24	2.40	2.55	2.88	3.24	3.64	4.13

Table 10. Values of k_s/k_u in benzene-diethyl ether mixtures.

Ether, wt.-%		0	8.2	16.6	34.7	54.4	75.9	100
p-Cl	0°	0.196	0.242	0.251	0.255	0.240	0.229	0.201
	15°	0.200	0.247	0.252	0.262	0.250	0.240	0.216
	25°	0.203	0.250	0.252	0.262	0.256	0.247	0.225
	30°	0.204	0.252	0.253	0.267	0.258	0.251	0.230
m-NO$_2$	0°	0.00371	0.00687	0.00679	0.00628	0.00513	0.00441	0.00387
	15°	0.00483	0.00824	0.00818	0.00772	0.00662	0.00581	0.00519
	25°	0.00567	0.00920	0.00917	0.00872	0.00774	0.00688	0.00621
	30°	0.00610	0.00969	0.00970	0.00925	0.00835	0.00747	0.00678
p-NO$_2$	0°	0.000320	0.000296	0.000285	0.000287	0.000211	0.000249	0.000206
	15°	0.000485	0.000481	0.000462	0.000478	0.000352	0.000427	0.000360
	25°	0.000625	0.000647	0.000621	0.000651	0.000482	0.000593	0.000505
	30°	0.000652	0.000744	0.000715	0.000754	0.000559	0.000695	0.000594

constant or can be neglected, a plot of ln (k_s/k_u) against the reciprocal of the dielectric constant of the medium should be a straight line of positive or negative slope depending on whether the substituent is electron-attracting or repelling. If the substituent is electron-attracting, k_s/k_u should increase with the temperature, and if it is electron-repelling, the reverse should be true.

The values of k_s/k_u calculated for the temperatures 0°, 15°, 25°, and 30° are given in Table 10. The rate constant values used were calculated from the Arrhenius equation. Fig. 5 shows that the plots of log (k_s/k_u) against $1/\varepsilon$ are not linear and that k_s/k_u decreases with increasing $1/\varepsilon$ only when the benzene concentration in the solvent is large. This implies that the non-electrostatic term $\Delta W/RT$ cannot be neglected.

The benzoylation of substituted anilines has previously been investigated in a number of pure liquids,[3] and it has been found[1] that the plots of log
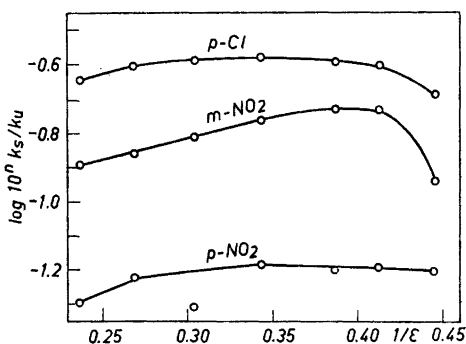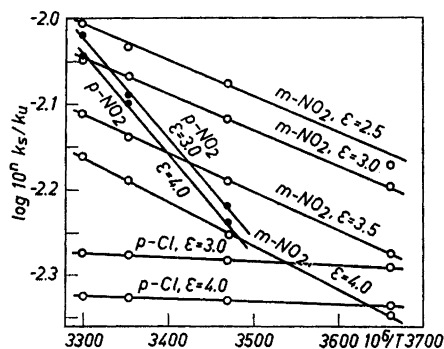

Fig. 5. Variation of log (k_s/k_u) with $1/\varepsilon$. Temperature 25°.

Fig. 6. Variation of log (k_s/k_u) $+n$ with $1/T$.

Table 11. Values of k_s/k_u for isodielectric benzene-diethyl ether mixtures.

		2.50	3.00	3.50	4.00
p-Cl	0°	0.236	0.256	0.242	0.231
	15°	0.252	0.262	0.247	0.234
	25°	0.253	0.265	0.250	0.237
	30°	0.254	0.267	0.253	0.237
m-NO$_2$	0°	0.00670	0.00637	0.00530	0.00445
	15°	0.00840	0.00764	0.00646	0.00557
	25°	0.00927	0.00855	0.00730	0.00647
	30°	0.00986	0.00895	0.00775	0.00692
p-NO$_2$	0°	0.000344	0.000285	0.000273	0.000254
	15°	0.000511	0.000475	0.000455	0.000406
	25°	0.000602	0.000646	0.000617	0.000504
	30°	0.000731	0.000755	0.000716	0.000622

(k_s/k_u) against $1/\varepsilon$ are approximately linear. A linear relationship prevails also between log (k_s/k_u) and $1/\varepsilon$ for the reactions in benzene-nitrobenzene mixtures.[1]

5. Substituent effects and temperature. The results in Table 10 show that the ratios k_s/k_u are dependent on temperature. Eqn. (2) implies that if the dielectric constant has the same value at all temperatures, ln (k_s/k_u) should increase or decrease linearly with increasing $1/T$ depending on whether δe_x is positive or negative. The ratios k_s/k_u computed for isodielectric benzene-ether mixtures are given in Table 11. Fig. 6 shows that the plots of ln (k_s/k_u) against $1/T$ are linear and have negative slopes which increase with the electron-attracting ability of the substituent, as required by eqn. (2).

6. The Hammett $\varrho\sigma$ relationship. The values of the Hammett reaction parameter ϱ (Table 12) were determined for the reactions in benzene-ether mixtures from the points for the benzoylation of aniline, p-chloroaniline, m-nitroaniline, and p-nitroaniline for which the fit to straight lines was relatively good. The σ values were taken from the book of Leffler and Grunwald.[19] Theoretically, if ΔW can be disregarded, the plots of ϱ against $1/\varepsilon$ at constant temperature should be linear. Actually curves similar to those in Fig. 5 are

Table 12. The values of ϱ under various conditions.

t	Ether, wt.-%, in the benzene-ether mixtures						
	0	8.2	16.6	34.7	54.4	75.9	100
0°	−3.09	−2.84	−2.82	−2.82	−2.94	−2.98	−3.11
15°	−2.97	−2.73	−2.72	−2.71	−2.80	−2.83	−2.94
25°	−2.90	−2.68	−2.67	−2.65	−2.72	−2.75	−2.84
30°	−2.88	−2.65	−2.64	−2.61	−2.65	−2.69	−2.79

Table 13. Values of ϱ for isodielectric benzene-ether mixtures.

t	ε			
	2.50	3.00	3.50	4.00
0°	−2.85	−2.82	−2.90	−2.97
15°	−2.71	−2.72	−2.78	−2.86
25°	−2.68	−2.64	−2.72	−2.80
30°	−2.63	−2.61	−2.68	−2.76

obtained (Fig. 7). On the other hand, when ε is kept constant (Table 13), the plots of ϱ against $1/T$ are linear (Fig. 8), in accordance with the results of Section 5.
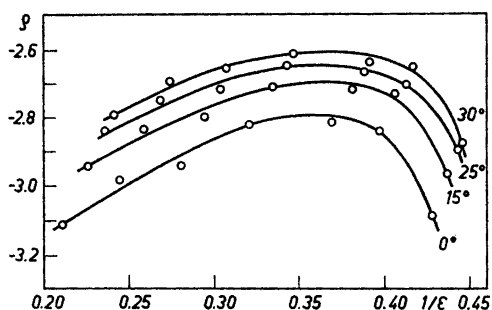
Fig. 7. Plot of ϱ against $1/\varepsilon$.
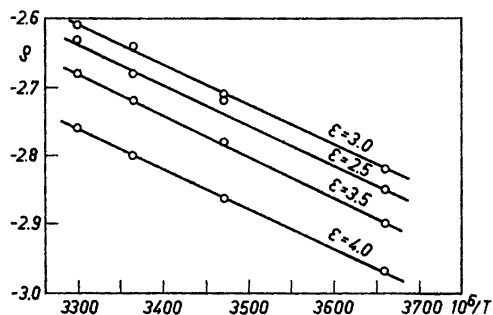
Fig. 8. Plot of ϱ against $1/T$.

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