XXXV.—*The Influence of the Polarity of the Solvent on the Velocity of a Reaction.*

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The purpose of this investigation was to examine the relationship between the influence which a solvent exerts on the velocity of a reaction and the polar properties of that solvent as measured by the electric moment of the molecule. For this purpose it was necessary to select solvents having similar constitutions but considerably different electric moments, and accordingly certain isomeric disubstituted benzene derivatives were chosen. The reaction between allyl bromide and pyridine appeared to be suitable for the study, since Hawkins (J., 1922, **121**, 1170) had already found for this reaction an approximate connexion between the influence of the solvent and the dielectric constant.

Experimental.

Satisfactory results were not obtained by the method given by Hawkins, and ultimately the following procedure was adopted. Solutions of pyridine (approx. $2M$) and of allyl bromide (approx. M) in the required solvent were prepared, and 2 c.c. of each were transferred by a calibrated pipette to a bulbed tube, which was rapidly sealed and placed in a thermostat, the time of insertion being taken as zero time for the reaction. After a definite interval the reaction was stopped by pouring the mixture into dilute nitric acid. The unchanged allyl bromide was removed by shaking with benzene, and the amount of quaternary compound formed was then determined by Volhard's thiocyanate method. The velocity coefficients were calculated from the equation $k=1/t(a-b) . \log_e b(a-x)/a(b-x)$; four or five determinations were carried out for each isomeride and the coefficients obtained were reasonably constant in all cases. Two examples of the results obtained are given below; a, b, and x (in g.-mols./l.) are respectively the initial concentrations of pyridine and allyl bromide and the concentration of the quaternary compound formed in time t (in minutes).

Solvent: benzene.
$a = 0{\cdot}979$; $b = 0{\cdot}496$.

t.	x.	$k \times 10^5$.
113	0·1331	304
158	0·1731	308
210	0·2109	308
257	0·2432	313
334	0·2788	305

Solvent: *m*-tolyl methyl ether.
$a = 0{\cdot}983$; $b = 0{\cdot}498$.

t.	x.	$k \times 10^5$.
26	0·1174	1122
34	0·1416	1102
41	0·1656	1105
48·5	0·1871	1102

A modified procedure was employed with solvents which were solid at room temperature and also where the amount of material available was small. Some of the solid was weighed into a tube and the calculated weight of pyridine was then added. The tube was placed in the thermostat and after the contents had melted the calculated volume of allyl bromide was added from a 1 c.c. graduated pipette. The contents of the tube were removed for analysis by washing out with hot benzene. For the calculation of the velocity coefficient, the volume of the solution was taken as the sum of the volumes of the solvent and of the two reactants. This method of procedure was not as accurate as the first, but a larger number of determinations were made and the average taken; thus, with *p*-nitrotoluene, $100k = 629$, 603, 589, 619, 628, 618.

All the solvents used, with the exception of *m*-dichlorobenzene, were B.D.H. reagents; the liquids were carefully fractionated and the solids recrystallised from alcohol. The *m*-dichlorobenzene was a sample from a previous research, and as only a small quantity was available it was not redistilled before use. Both the pyridine (b. p. 116·8° after refluxing over caustic potash) and the allyl bromide (b. p. 69·8—70·0°) were kept in the dark and remained colourless throughout the experiments.

The results are summarised in Table I. The velocities of reaction in the corresponding monosubstituted derivatives as solvents have also been determined under the same conditions, and are included for comparison. In the second column are given the ranges of x for which the reaction has been investigated, in the third the extent of variation of k obtained, in the fourth the average value of k, and in the last there are reproduced the figures for the electric moment, μ, found by Smyth and Morgan (*J. Amer. Chem. Soc.*, 1928, **50**, 1544) and Williams and Schwingel (*ibid.*, p. 366). All experiments were carried out at 56·4° ± 0·1°.

TABLE I.

Solvent.	x.	$k \times 10^2$ (range).	$k \times 10^2$ (mean).	$\mu \times 10^{18}$.
Benzene	0·133—0·279	0·304—0·313	0·308	0·20
Chlorobenzene	0·106—0·255	0·917—0·940	0·924	1·56
o-Dichlorobenzene	0·119—0·201	1·533—1·588	1·566	2·25
m- ,, ,,	0·102—0·143	0·847—0·886	0·866	1·48
p- ,, ,,	0·131—0·171	0·792—0·812	0·799	0·00
Anisole	0·168—0·268	1·545—1·605	1·581	
o-Tolyl methyl ether	0·082—0·190	0·822—0·835	0·829	
m- ,, ,,	0·117—0·187	1·102—1·122	1·108	
p- ,, ,,	0·115—0·199	1·087—1·120	1·103	
Nitrobenzene	0·355—0·395	9·70—10·52	10·15	3·90
o-Nitrotoluene	0·313—0·432	5·902—6·100	5·993	3·75
m- ,,	0·297—0·371	4·646—4·872	4·841	4·20
p- ,,	0·322—0·431	5·891—6·290	6·145	4·50

Discussion of Results.

Consideration of the above results shows that in certain cases the marked differences found in velocity in the isomerides can be explained by the size of the moment of the molecule. For instance, *m*-dichlorobenzene has approximately the same moment as chlorobenzene and the rate in the two solvents is nearly equal; on the other hand, the *o*-isomeride has a greater moment and the velocity is correspondingly increased. Although no values for the moments of the tolyl methyl ethers are yet available, the dielectric constants as determined by Philip and Haynes (J., 1905, **87**, 1000), *viz.*, *o*- = 3·57, *m*- = 4·08, *p*- = 4·03, show that the velocities in these isomeric solvents are also in striking accord with their polar nature. In other cases, however, variations occur in the velocity which would not be expected from the moments; *e.g.*, *p*-dichlorobenzene has zero moment which leads one to predict a velocity in it comparable with that in benzene, whereas actually the value found is more than twice as great. Similarly there is no evidence from the moments of the molecules to account for the rate in *m*-nitrotoluene being markedly lower than in its two isomerides.

The conclusion may be drawn, therefore, for these isomerides that in some cases the influence of the solvents can be connected satisfactorily with the moments of their molecules, but that in other cases differences of velocity occur which are not due to changes in the molecular moments.

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